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THE
PHYSICAL REVIEW

X-RAY WAVE-LENGTH CHANGE BY PARTIAL ABSORPTION

By J. M. Cork
University of Michigan
(Received May 11, 1931)

Abstract

The attempt to repeat the experiments of Mr. B. B. Ray in which a change in wave-length occurred in an x-ray beam upon passage through an absorbing substance, has been continued. In the previously reported experiments CuK radiation was passed through absorbers of boron, beryllium, carbon, nitrogen and oxygen. These same absorbers have been retried with tungsten L radiation with a spectrometer of greater dispersion. Although it should have been possible to observe a modified line of 1/3000 the intensity of the unmodified, in no case has any trace of a modified line been observed.

WHEN x-rays are incident upon matter they react with the electrons of the matter in various possible ways. One type of interaction, the photo-electric effect, in which the x-ray photon communicates all its energy to the electron, ejecting it from the atom, the remainder of the energy of the photon appearing as the kinetic energy of the electron, is now well established. Equally well established is the Compton effect in which the photon interacts with the free electron giving a portion of its energy to the electron, which is ejected as a recoil electron. The emergent photon with lessened energy is consequently of longer wave-length. For electrons bound in definite energy states a fine structure of the scattered modified photon on the long wave-length side would appear as a possibility. Recent experiments[1] indicate that this fine structure does not exist.

Observing the failure of these experiments, Mr. B. B. Ray[2] examined the wave-length of the emergent photons for zero scattering angle. For this angle the Compton wave-length shift would be zero. A spectral photograph of the transmitted beam showed along with the strong line due to the unmodified incident wave-length, certain fainter companion lines displaced toward longer wave-lengths. The displacements of these lines as reported, were just as would be expected if in the passage through the absorbing substance the photon gave up some of its energy to elevate a bound inner electron to an outer energy level, passing on unchanged in direction but with less energy and hence longer wave-length.

[1] Ehrenberg, Zeits. f. Physik **53,** 234 (1929); Coster, Nature **123,** 642; Kast, Zeits. f. Physik **58,** 519 (1929); Bearden, Phys. Rev. **36,** 791 (1930); Gingrich, Phys. Rev. **36,** 1050 (1930).

[2] Ray, Nature **125,** 746 and 856; **126,** 399; Zeits. f. Physik **66,** 261 (1930).

Thus the energy equations may be shown:

Photoelectric effect	$h\nu = h\nu_e + (1/2mv^2)$ photoelectron	(1)
Compton effect	$h\nu = (1/2mv^2)$ recoil electron $+ h\nu$ mod.	(2)
Ray effect	$h\nu = h\nu_e + h\nu$ mod.	(3)

The existence of this last effect is thus of such importance that the experiments seemed worthy of repetition.

Experimental

To this end an attempt was made to repeat the work of Ray. The first experiments[3] using a copper target x-ray tube equipped with a Lindemann thin glass window with a calcite crystal spectrometer were carried out in the laboratory of Dr. M. deBroglie in Paris. The investigation has been continued in this university using both copper and tungsten target tubes with a calcite crystal spectrometer having slit-crystal and crystal-photographic plate distances of 54 cm. This gives a dispersion on the photographic plate of about 5 x.u. per mm.

The absorbing layer was in every case placed between x-ray target and spectrometer slit. Various thicknesses of material were employed although the thicker the material the more apparent the effect should be. The absorbing layers used by Ray were not well described in his reports, except that he mentions the use of lamp black for carbon[4] absorption. Besides carbon, absorbing layers of beryllium, boron, nitrogen and oxygen have been used. Screens made of various thicknesses of gold beaters skin have also been tried.

In order to form an estimate of relative intensities a portion of the unmodified line was covered with a shield during most of the exposure. This shield for a twenty hour exposure was generally removed only for 2 minutes. The intensity of radiation was such that generally an exposure of 2 seconds was enough to render the main unmodified line visible.

In these experiments the crystal was kept stationary during two exposures, first with and then without absorber in place.

Results

Using the various absorbers mentioned, no trace whatever of a modified line in the positions to be expected was observed. Typical spectrograms obtained are shown in Fig. 1. For these spectrograms the target was of tungsten, giving the strong line W$L\alpha_1$, and also the $L\alpha_2$ line whose intensity is about one-tenth as strong. The copper K lines always appeared unintentionally on the same plate, due presumably to a copper focussing cylinder on the cathode. On certain of these prints even the very faint Cu$K\alpha_3$, α_4 line is observable, although its intensity is only about 1/600 that of the Cu$K\alpha_1$ line.

The intensity of the modified line as observed by Ray was about 1/400 that of the parent line. In these spectrograms shown in Figure 1 the intensity

[3] J. M. Cork, Comptes Rendus, Acad. Sci. Paris, 192, 153.

[4] In a letter to the writer Mr. Ray mentions that 4 or 6 thicknesses of gold beater's skin gave equally good results.

of the W$L\alpha_2$ line on the shielded part of the figure is about 1/6000 that of the unshielded W$L\alpha_1$. Now a line of the intensity of the W$L\alpha_2$ line located in the region of general blacking on the plate might be somewhat obscured.

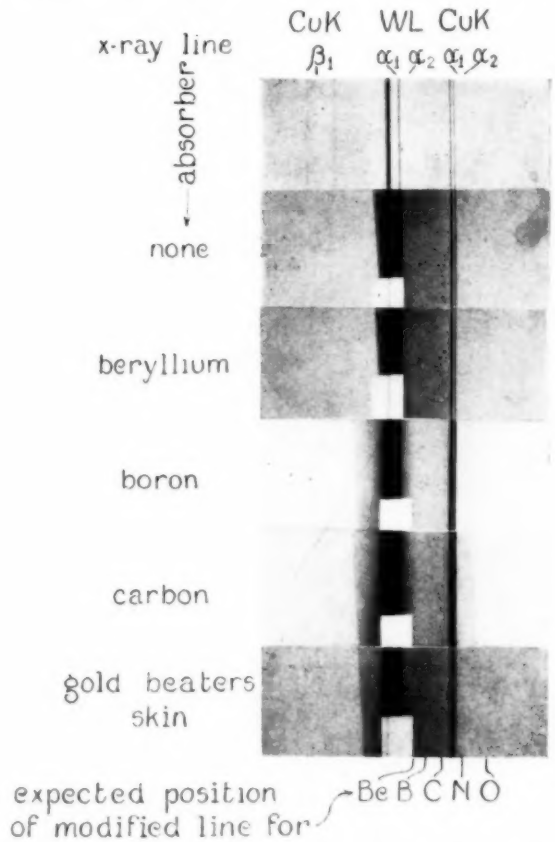

Fig. 1. Showing the absence of expected modified lines.

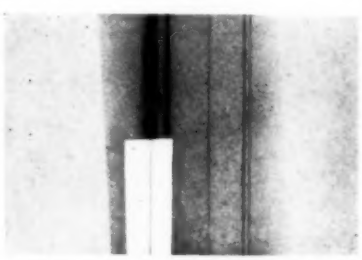

Fig. 2. Showing superposition of W$L\alpha_1$, α_2 2 min. Exposure on general radiation exposure 20 hours.

However, if the general blackening is not too strong it offers but slight hindrance to the observance of relative intensities. This is illustrated in Fig. 2. In this figure after the exposure was completed with shield in place twenty

hours and then removed for two minutes, the whole plate was shifted along and the lines allowed to fall in the region of general radiation for a period of two minutes. One observes little loss in contrast.

If the effect exists therefore, it must be of an intensity much less than that reported by Ray. Other experimenters[5] have now likewise failed to observe the modified lines, although their existence has been confirmed by others.[6]

This opportunity is taken to express appreciation to M. deBroglie for the generous facilities of his laboratory and to M. Thibaud and M. Duprés la Tour for their kind assistance during the first part of this investigation.

[5] G. A. Lindsay, Nature **127,** 305. J. H. Van der Tuuk, Naturwissenschaften **14,** 308. A. J. O'Leary, Phys. Rev. **37,** 873 (1931).

[6] Majumdar, Nature **127,** 92. Ray states in his letter that the effect has been observed by Prof. Saha at Allahabad University.

STRUCTURE OF THE HELIUM ARC LINE 3888*

By R. C. Gibbs and P. G. Kruger
Physical Laboratory, Cornell University

(Received April 24, 1931)

Abstract

The helium arc line ($1s2s\ ^3S_1 - 1s3p\ ^3P^\circ_{0,1,2}$)3888A, has been examined for structure and has been resolved into the three components which are predicted by theory. The $1s3p\ ^3P^\circ_{0,1,2}$ levels are inverted which is in agreement with previous results for the $1s2p\ ^3P^\circ_{0,1,2}$ levels. The frequency differences in the present case are:

$$\nu_{0,1} = 0.192 \text{ cm}^{-1}, \qquad \nu_{1,2} = 0.165 \text{ cm}^{-1}.$$

Introduction

In 1927 Houston[1] reported the structure of the $1s2p\ ^3P^\circ_{0,1,2}$ levels. Later in the same year G. Hansen and P. G. Kruger[2] finished the analysis of the He arc lines 5876, 4713 and 4472, thus completing the term scheme for $1s2p\ ^3P^\circ_{0,1,2}$ and $1s3d\ ^3D_{1,2,3}$. No attempt was made at that time to determine the structure of higher P° terms.

Experimental

The line 3888A $1s2s\ ^3S_1 - 1s3p\ ^3P^\circ_{0,1,2}$ is one of the strongest lines of the He I spectrum and was easily excited in a metal liquid-air cooled Schüler lamp. A Fabry-Perot interferometer with 5 mm, 8 mm, and 10 mm spaces between the mirror surfaces was used to analyze the line. Mirrors having a reflection coefficient of 92 percent were used so that the resolving power varied from 0.775×10^6 to 1.55×10^6 as the distance between the mirrors was increased from 5 mm to 10 mm.

Results

Table I. *Components of the helium line* 3888.

Int.	λ	Δλ	ν	Δν
10	0.0000A		0.000 cm^{-1}	
		0.0247A		0.165 cm^{-1}
7	−0.0247		0.165 cm^{-1}	
		0.0298		0.192 cm^{-1}
3	−0.0545		0.357 cm^{-1}	

Table I gives, in column one, the relative estimated intensities of the components as obtained from several microphotometer curves made from

* The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher. Acknowledgment is also made of the use of spectroscopic apparatus which was in part purchased by a grant from the National Research Council.

[1] Houston, Proc. Nat. Academy **13,** 91 (1927).

[2] Published by G. Hansen, Ver. Deut. Phy. Ges. **10,** 5 (1929).

various plates. The wave-lengths (assuming the strongest line zero), wave-length separations, frequency numbers and frequency separations are given in columns 2, 3, 4 and 5 respectively.

Fig. 1 shows a microphotometer curve of one of the plates.

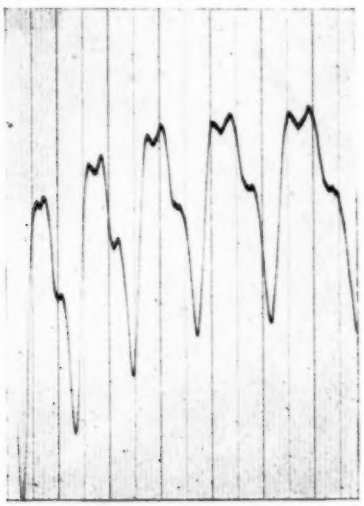

Fig. 1. Microphotometer curve showing the structure of the He arc line 3888.

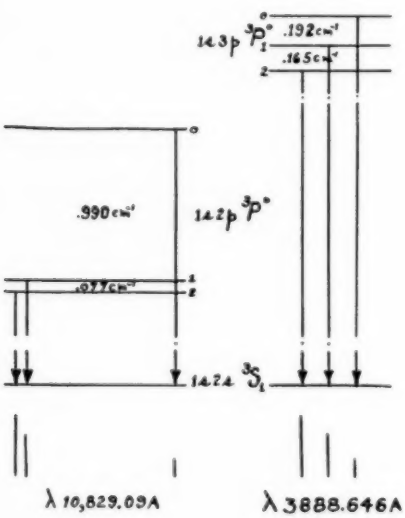

Fig. 2. Term separations for the first two members of the $1snp\ ^3P^\circ$ series in helium, He I.

Fig. 2 shows the term scheme for the $1s2p\ ^3P^\circ_{0,1,2}$ and $1s3p\ ^3P^\circ_{0,1,2}$ terms with respect to the $1s2s\ ^3S_1$ term. The relative separations of the two $^3P^\circ$ terms are drawn to the same scale.

Discussion

It is interesting to note that the anomalous separations of the $1s2p\ ^3P^\circ$ terms are no longer so anomalous in the $1s3p\ ^3P^\circ$ terms. In the latter case the separations are more nearly what would be expected if the Landé interval rule were obeyed. Thus if the $^3P^\circ$ term separations continue to become more normal in higher total quantum states the $1s4p\ ^3P^\circ$ terms should have nearly a 2:1 separation.

Resolution of the structure of the line 3187A ($1s2s\ ^3S_1 - 1s4p\ ^3P^\circ_{0,1,2}$) would show whether the separation of the $1s4p\ ^3P^\circ$ terms have a 2:1 ratio. Assuming that the rate of decrease of $\Delta\nu_{0,2}$ between the first and second members of this series of terms is continued to the third member, a value of about 0.120 cm^{-1} is computed for $\Delta\nu_{0,2}$ for the $1s4p\ ^3P^\circ_{0,1,2}$ terms. Thus if the 2:1 ratio exists in the third member, the components of the 3187 line would be 0.0082 and 0.0040A apart. The complete resolution of components lying as close together as this necessitates cooling the discharge in liquid hydrogen or preferably in liquid helium. It is hoped that some other laboratory in which these low temperatures are available will undertake to study the structure of this line.

In 1926 Heisenberg[3] calculated the separation of the $1s2p\ ^3P^\circ_{0,1,2}$ term and obtained results which were later found to be in agreement with experimental results.[1,2] It would be desirable now to have the $1s3p\ ^3P^\circ_{0,1,2}$ term separations calculated by quantum theory or wave mechanics to see if the agreement here is as good as in the previous case.

A possible reason why the P° term separations in higher quantum states should approach the normal 2:1 ratio, is that in the higher quantum states the p electron is less tightly bound to the nucleus and thus the energy conditions in these higher states are more nearly like those in heavier elements. Furthermore the coupling of the np electron to the $1s$ electron becomes weaker in the higher quantum states,—so that possibly with increasing n the interaction arising from the action of the orbital motion or the spin of one electron on the spin of the other becomes less effective in determining the internal ratio.

[3] W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

RAMAN SPECTRA OF SULPHURIC ACID

By Raymond M. Bell and W. R. Fredrickson
Pennsylvania State College and Syracuse University

(Received May 11, 1931)

Abstract

Concentrated H_2SO_4 gives a series of Raman lines which, with the exception of the 4566A line, decrease in number and intensity with a decrease in concentration and finally disappear. At the point at which the above lines vanish, a broad line (4817A) appears and persists in dilute solutions. At low concentrations the water bands are present. The 4566A line is present at all concentations of acid and increases in intensity with a decrease in concentration, but is missing in pure water. A line with the same wave-length (within experimental error) and intensity variation is found in HNO_3, and it is suggested that the two lines have the same origin.

RAMAN spectra have made possible a new approach to the study of conditions in acids at various dilutions. Rao[1] found that the Raman lines obtained from HNO_3 could be classified into the three following groups according to their behavior as the acid was diluted: (1) those due to the HNO_3 molecule, (2) those due to the NO_3^- ion, and (3) those due to the water molecule. The lines of the first group decrease in intensity as the concentration is decreased and finally disappear. The lines in the second group increase in intensity as the concentration is decreased, reaching a maximum at the concentration when the lines of the first group vanish, and then these lines also decrease in intensity. The lines of the third group appear as bands which first appear faintly as the acid is somewhat diluted and gradually increase in intensity and broaden as the concentration is decreased. The purpose of this paper is to present similar data obtained from sulphuric acid at various dilutions. A preliminary account of data has previously been reported in a letter to Nature.[2]

The method used to obtain spectrum was similar to the general method described by R. W. Wood,[3]—using a mercury arc. Most of the photographs were taken with a prism spectrometer, but plates were also obtained with a plane grating on the spectrometer table in place of the prism. The latter arrangement gave greater dispersion, but the intensity was, indeed, greatly reduced.[4] Definite traces of lines and bands were found at all concentrations. With the prism, most of the lines could be obtained with an exposure of three minutes and the strongest could be detected on plates of a minute exposure. The lines in Table I are all taken from plates with 30 minute exposure,—

[1] Rao, Proc. Roy. Soc. **A127,** 279 (1930).
[2] Bell and Fredrickson, Nature **125,** 895 (1930).
[3] R. W. Wood, Phil. Mag. **6,** 729 (1928).
[4] Attempts were made to obtain Raman spectra with a small concave grating of 120 cm focus, but without success.

with experimental conditions exactly the same throughout. A fifteen hour exposure with the grating gave the same intensity as the thirty minute prism exposure and those lines are listed in Table II. The concentrations are measured in mol percent. That is, 50 percent concentration is one H_2SO_4 molecule to one H_2O molecule; 100 percent is the purest acid available, commercial 96 percent; and 0 percent is pure distilled water. The wave-lengths are accurate to 3A. The numbers in parentheses are eye estimates of the intensity of the lines.

TABLE I. *Raman spectrum of H_2SO_4 (Prism).*

Concentration (percent)	Wave-length in Angstroms						
100			4585 (1)	4566 (1)	4542 (4)	4470 (3)	4438 (3)
90				4566 (1)	4542 (3)	4470 (3)	4438 (3)
80				4566 (2)	4542 (3)	4470 (3)	4438 (3)
70				4566 (2)	4542 (2)	4470 (2)	4438 (2)
60				4566 (2)	4542 (2)	4470 (2)	4438 (2)
50				4566 (3)	4542 (1)	4470 (2)	4438 (2)
40	4817			4566 (3)	4542 (1)	4470 (2)	4438 (2)
30	4817			4566 (3)			
20	4817	4750 to 4700		4566 (3)			
10	4817	4750 to 4700		4566 (2)			
0		4750 to 4700					

100	4276 (0)	4252 (0)	4224 (3)	4203 (4)	4171 (0)	4142 (2)	
90			4224 (3)	4203 (3)	4171 (0)		
80			4224 (3)	4203 (3)			
70			4224 (2)	4203 (2)			
60			4224 (2)	4203 (1)			
50			4224 (1)	4203 (1)			
40			4224 (1)	4203 (0)			
30							
20			4225 to 4175				
10			4225 to 4175				
0			4225 to 4175				

Notes. 4817 was a broad line or band at all times.
4566 became broad at low concentrations.
4750 to 4700 and 4225 to 4175, water bands, became sharper and less intense as concentration increased.

TABLE II. *Raman spectrum of H_2SO_4 (Grating).*

Concentration (percent)	Wave-length in Angstroms							
100	4585 (1)	4566 (1)	4540 (4)	4470 (3)	4440 (2)	4279 (0)	4225 (1)	4203 (2)
80		4566 (2)	4540 (3)	4470 (3)	4440 (2)		4225 (1)	4203 (1)
60		4566 (3)	4540 (3)	4470 (3)	4440 (2)		4225 (0)	4203 (1)
40		4566 (4)	4540 (2)	4470 (3)	4440 (2)		4225 (0)	4203 (0)
30		4566 (3)	4540 (1)	4470 (1)	4440 (1)		4225 (0)	4203 (0)

From Table I we see that the lines found in concentrated H_2SO_4 persist as far down as 40 percent. The lines given for 100 percent agree with the re-

sults obtained by Ganesan and Venkateswaran[5] with concentrated H_2SO_4. The intensity of all lines except the 4566 line decreases in intensity with a decrease in the concentration. The 4566 line, however, increases in intensity to a maximum and then broadens and decreases in intensity. The two water bands are in approximate agreement with the measurements given by others. It is interesting, however, to note the decrease in breadth and the sharpness of these bands at their first appearance at high concentrations. The origin of the 4817 line or band is uncertain. It makes its appearance when the other lines disappear and is always broad. The 4470 line is the only one which seems to indicate a shift in wave-length as the concentration is decreased. On some of our plates there is a slight indication that this line has shifted slightly to the red.

The lines obtained with the grating, as listed in Table II, are similar to those in the preceding one. Here even the 30 percent concentration shows some of the H_2SO_4 molecule lines. The most striking thing about the grating plates is the change in intensity with concentration. The 4540 line decreases considerably in going from 100 to 40 percent, while the 4566 line increases correspondingly.

Comparing the above results with those reported by others we find two interesting facts. (1) Several experimenters[6] working with sulphates find in all cases lines at 4552A and 4214A which they attribute to the $SO_4^=$ ion. Our plates fail to reveal these lines, not even the plates of very long exposure time. (2) Rao[7] reports a line at 4567A which he finds at all concentrations of HNO_3. We also find a line at 4566A which appeared at all concentrations. Ganesan and Venkateswaran[8] give 21895 cm^{-1} as the measurement for the same H_2SO_4 line and 21893 cm^{-1} for the HNO_3 line. Both of these lines increase in intensity with a decrease in concentration. Neither line appears in pure distilled water. We are inclined to believe that this close agreement in wave-length and variation in intensity with concentration is not fortuitous, but rather an indication that the two lines may have the same origin—perhaps a hydrated hydrogen ion.

The experimental work described above was done in the Department of Physics at Syracuse University.

[5] Ganesan and Venkateswaran, Ind. Jour. of Phys. **4,** 195 (1929).

[6] Mukherjee and Sen Gupta, Ind. Jour. of Phys. **3,** 503 (1929). Hollaender and Williams, Phys. Rev. **34,** 994 (1929).

[7] Rao, reference 1.

[8] Ganesan and Venkateswaran, reference 5.

INVESTIGATIONS IN THE SPECTRAL REGION BETWEEN 20 AND 40μ

By John Strong*
California Institute of Technology, Pasadena

(Received May 5, 1931)

Abstract

An apparatus is described which is convenient for studying the optical properties of substances with reststrahlen having wave-lengths from 6 to 150μ. A vibrationless support is described, the essential features of which are copied from the design of R. Müller but the construction is simplified. The transmission of several gases was studied with reststrahlen having wave-lengths 20 to 33μ. SO_2 shows strong absorption at 20.75μ. The reflectivity of SO_2 was tested and found to be zero at both 20.75μ and 8.7μ where it has strong absorption bands. Gas absorptions from 20 to 33μ are compared with the Raman indications. Transmissivities and reflectivities of various materials are given for the spectral region 20 to 33μ. β—MgO was found to have a reststrahlen near 23μ. Potassium iodide was found to be transparent to wave-lengths greater than 33μ.

THE region of the spectrum between 20 and 40μ has not been as extensively investigated as the regions on either side, due to the lack of materials having suitable optical properties for windows, dispersing prisms and filters. The use of various reststrahlen and gratings with open thermocouples (or microradiometers) has given us most of the knowledge we have of the optical properties of substances in this region. Recently, L. Kellner[1] has studied the transmission of paraffin (Kahlbaum M.P. 68°–72°C) and found that layers of 1.2 mm thickness are sufficiently transparent beyond 20μ for use as thermocouple windows. This discovery materially decreases the difficulty of investigation in this region.

Potassium chloride is transparent to 23μ, potassium bromide to 30μ, and potassium iodide to wave-lengths greater than 33μ. The technique for growing large crystals of these materials was developed by the author[2] at the University of Michigan. With these materials available the region now open for prism spectroscopy extends beyond 15μ by more than an octave of frequencies. The purpose of this present paper is the extension of our knowledge of the optical properties of substances in this new region.

Schaefer and Matossi[3] have prepared a table of the reststrahlen bands which have well established wave-lengths. Several of these bands fall in the spectral region 20–40μ and the present investigation was made with these bands.

The reststrahlen bands are not as monochromatic as might be desired but this is compensated for by the abundance of available energy and the

* National Research Fellow.

[1] L. Kellner, geb. Sperling, Zeits. f. Physik **56,** 215 (1929).

[2] John Strong, Phys. Rev. **36,** 1663 (1930).

[3] Schaefer and Matossi, Das Ultrarote Spektrum, p. 60 (1930).

wide range of wave-lengths which are obtainable with the one technique. Wave-lengths from 6 to 150μ are thus obtainable, corresponding to a frequency range of more than five octaves.

The Apparatus

A reststrahlen apparatus was devised for these experiments which was superior to older reststrahlen arrangements in the following ways. First, the crystal reflectors needed were of small size and, consequently, easier to obtain than the large crystals required for the old arrangements. Second, the transfer of crystals in going from one wave-length to another was a simple operation requiring only a few seconds of time and this operation did not disturb the air through which the radiations passed and thus it was possible to keep the air dry at all times.

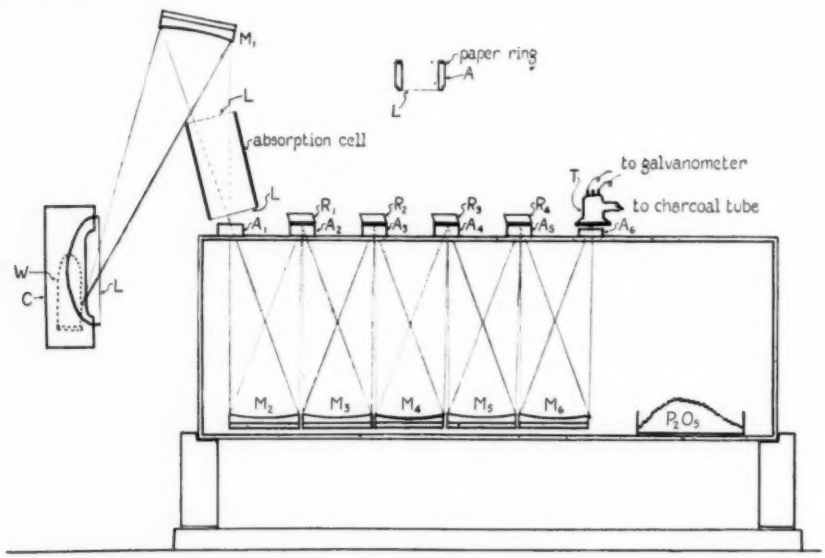

Fig. 1. Diagram of reststrahlen apparatus.

Fig. 1 is a diagram of the reststrahlen apparatus used for this research. Light from the Welschback mantle is reflected by the mirror, M_1, into the reststrahlen apparatus through the circular hole, A_1, where it subsequently passes, after reflection from the concave spherical mirror, M_2, to a second circular hole, A_2. A crystal mirror, R_1, covers this hole and reflects the light to the concave mirror, M_3, where it is returned for the second reststrahlen mirror, R_2. After three (or four) successive reflections from reststrahlen mirrors and possibly one reflection from a metal mirror, the light is focused onto the receivers of the vacuum thermocouple, T. The thermocouple is a compensated two junction type, with one of the junctions covered by a rocksalt plate. This thermocouple was made for me by Dr. C. H. Cartwright. The window for the thermocouple was a 1 mm plate of potassium iodide.

For studying the absorption of gases, an absorption cell may be introduced into the radiation path between the mirror, M_1, and the circular hole, A_1.

The housing for the reststrahlen apparatus is made from brass sheet laid over a framework of half inch square iron rod. This is mounted on a wooden support. The corners were sealed with beeswax to make the apparatus gas tight so the air might be dried with P_2O_5. The base of the housing was penetrated by three adjusting screws (not shown) for each of the spherical mirrors, M_2 to M_6. The outside of the housing was covered with a layer of felt and to protect further the apparatus from temperature fluctuation, it was encased within galvanized iron walls. The insert, A, in Fig. 1 shows a cross section of one of the small brass cylinders which fit over the holes A_1 to A_5. This is drawn to a scale twice as large as that for the rest of the figure. The cylinders each have a lacquer window, L, stretched over their base.

These lacquer windows are very transparent (96 to 100 percent) for waves longer than 20μ and permit the air within the apparatus to be kept dry, when the reststrahlen mirrors are being interchanged. A paper ring on the top of each cylinder protects the mirrors from being scratched.

Because the silver mirrors are not used on their optical axes, there is considerable astigmatism. This results in a large final image with smaller intensity than if there were no astigmatism. The illumination in the center of the final image will increase, however, as the size of the reststrahlen mirrors is increased. It is believed that since the reststrahlen surfaces used were each $\frac{3}{4}$ inches in diameter, the illumination of the thermocouple receivers was not greatly attenuated due to astigmatism.

In order to have the galvanometer free from microseismic vibrations, it was mounted on a vibrationless support. This support was a simplification of the one designed by R. Müller,[4] and was constructed in the following manner. Three triangular plywood boards, each $\frac{1}{2}''$ thick and $11''$ on an edge were clamped and bored with six $\frac{3}{8}''$ holes, two holes in each corner. (See Fig. 2). The two upper triangles were separated $20''$ and bolted together at this distance with three $\frac{3}{8}''$ brass rods, one at each corner, to form the swinging framework for the galvanometer. The top and bottom plywood triangles were fastened together by three $24''$ brass rods $3/32''$ diameter. These rods passed freely through the remaining $\frac{3}{8}''$ holes in the middle triangle. The bottom triangle served for the base of the support while the $3/32''$ rods afforded the necessary looseness of mechanical connection between the swinging framework and the earth. Three levelling nuts screw on the termini of the $3/32''$ rods below the bottom triangle. Four $10''$ pie pans are filled with transformer oil and stacked on top of the swinging framework to dampen oscillations. These pans were filled to the depth found by experiment to give maximum damping. The galvanometer was mounted on the middle triangle and above it on a tripod ballast was placed to make the period of oscillation of the support about two seconds. When this period is attained, the mechanical coupling is sufficiently loose to isolate effectively, the galvanometer from the horizontal components of microseismic vibrations. No protection against vertical components is necessary as these do not cause a spurious deflection

[4] R. Müller, Ann. d. Physik **1**, 613 (1929).

of the galvanometer. In order to clamp rigidly the support for making adjustments, tapered pins are dropped along the side of the 3/32″ rods in two of the holes in the middle plate. The swinging framework suffers a slight parallel displacement when these pins are removed but this does not affect the galvanometer adjustment. This support is conveniently housed on a corner shelf to shield it from air currents.

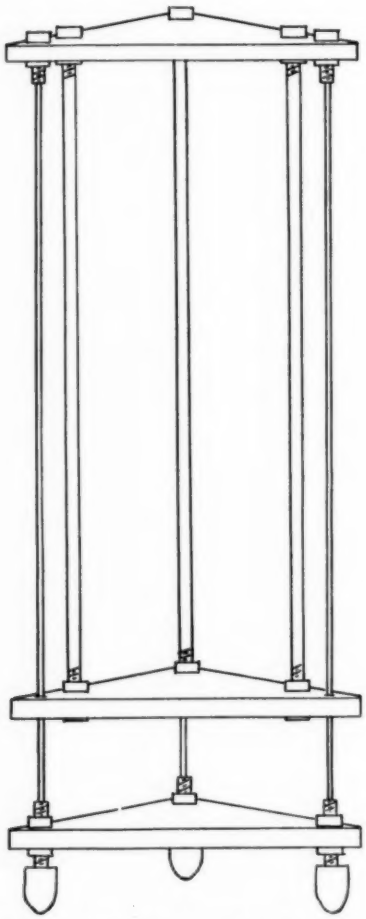

Fig. 2. Vibrationless support for galvanometer.

In order to shield the Welschback mantle, *W*, from air currents, a lacquer film, *L*, was stretched across the opening of the water-cooled chamber, *C*, which surrounds it. The radiations were taken off at nearly grazing incidence because the mantle was porous. Although the mantle material is quite opaque to waves 20–40μ, the mantle at normal incidence, showed an absorption of only 70 percent for these radiations due to its porosity.

The thermocouple receivers were blackened with a paint made from pulverized mantle material and colorless lacquer. Tests showed that these re-

ceivers absorbed as much as when coated with a mixture of soot and water glass but the paint did not cause the receivers to curl as water glass did.

The Reststrahlen

The table of Schaefer and Matossi is reproduced in part. This gives the method used for obtaining reststrahlen having wave-lengths of 20 to 33μ.

Table I.

Substance	Number of reflections	Filter	λ	*E*	Literature
Quartz	4	2.5 mm AgCl	20.75μ 8.7 μ	18.0 12.0	H. Rubens and E. F. Nichols, Wied. Ann. **60**, 418 (1897).
Fluorite	3	5 mm KCl	22.9 μ	6.0	H. Rubens Berl. Ber., 1915, p.4.
Calcite Fluorite	2 2	3 mm KBr	27.3 μ	8.0	H. Liebisch and H. Rubens, Berl. Ber., 1919, p. 876.
Marble	4		29.4 μ 6.7 μ	14.0 4.0	E. Aschkinass, Ann. d. Physik **1**, 42, (1900).
Fluorite	3	0.4 mm SiO_2 1.2 mm KBr	32.8 μ	0.75	H. Rubens, Wied. Ann. **69**, 576 (1899).

The numbers given in column *E* represent the observed galvanometer deflection in centimeters for the various reststrahlen. A Leeds and Northrup high sensitivity galvanometer was used with the scale at 3 meters. In order to eliminate shorter waves as much as possible a soot filter was used and these values are for the energy transmitted by this filter.

In the present experiments a 1 cm KCl filter was substituted for the 2.5 mm AgCl filter recommended by Rubens and Nichols. This is justified by the transmission curves given by Rubens and Trowbridge[5] for AgCl and KCl.

In the present experiments, the 27.3μ rays were not polarized as specified by Liebisch and Rubens and it was not possible to test the wave-length of the rays to find the effect of this omission.

The 32.8μ rays were apparently homogeneous for the transmission of a KBr plate. 1.2 mm thickness was found to be 68 percent while Rubens states that it transmits more than $\frac{2}{3}$ of the 32.8μ reststrahlen.

Except for the 20.75μ and 29.4μ reststrahlen a rocksalt shutter of 3 mm thickness was used. For these reststrahlen both rocksalt and metal shutters were used. If E_T was the energy of both reststrahlen and A_T was the absorption of the sample for this energy, then if E_s was the energy passed by a rocksalt filter, i.e., the energy of the short reststrahlen, and A_s the part of this energy absorbed by the sample, then, allowing 9/10 as the transmission of the rocksalt shutter for the short waves, the long wave (i.e. the 20.75 and 29.4μ reststrahlen) energy is $(E_T - E_s/0.9)$ and the long wave energy absorbed by the sample is $(A_T - A_s/0.9)$.

[5] H. Rubens and A. Trowbridge, Wied. Ann. **60**, 724 (1897).

Measurements

Gases. The gases used for the present measurements were not especially purified. They were drawn from stock cylinders or were the vapors of chemically pure liquids. The chief difficulty in obtaining consistent results was due to the variable concentration of vapor within the absorption cell. Benzene and CCl_4 were observed to wet the lacquer windows at times and this gives an indication that these liquids would, in all probability, be transparent. The values given in Table II are averages of four to eight independent runs taken on different days and are thought to be correct to about 2 percent. They are slightly different from some preliminary results published in a Letter to the Editor. These differences in some cases are due to additional data but for the wave-lengths 20.75 and 29.4μ the differences are due chiefly to corrections for the transmissivity of the rocksalt filter used.

Table II. *Percent transmission.* (*Length of cell*, 4 *inches*).

Material	Pressure Millimeters	6.7μ	8.7μ	20.75μ	22.9μ	27.3μ	29.4μ	32.8μ
NH_3	760	24	26	79	93	83	82	62
N_2O	760	102	77	90	100	101	101	102
C_2H_2	760	95	92	99	101	101	100	98
H_2S	760	97	98	98	97	92	90	83
SO_2	760	98	5	7	58	100	100	96
C_6H_6	96	65	97	102	99	100	98	95
CCl_4	114	95	99	97	99	99	99	91
CS_2	361	30	98	100	86	98	99	96
$CHCl_3$	200	93	90	99	98	98	97	97
$(C_2H_5)_2O$	526	17	6	61	45	69	71	61

The gradual decrease of transparency for H_2S and N_3H at longer wave-lengths may be due to the short wave-length end of the pure rotation spectrum.

The only strong absorption band discovered in the new spectral region was for SO_2 at 20.75μ. This band agrees with Raman indications[6] and is possibly the third fundamental band for SO_2. The strong absorption of SO_2 for both the reststrahlen of quartz is quite striking. The absorption cell filled with SO_2 cuts off these radiations almost the same as a metal shutter.

R. W. Wood[7] has shown that the mercury line 2536 is reflected by hot mercury vapor at a high pressure. He states "It appeared highly probable that if the molecular resonators were packed closely enough together, the secondary wavelets which they emit, having a definite phase relation would unite into a single wave, and the scattered light would disappear, regular reflection taking its place." Because of the strong absorption of SO_2 for the reststrahlen of quartz it was decided to test this hypothesis. High pressures should not be necessary on account of the long wave-lengths involved. Accordingly, a cell was fitted with a window of KBr and one of the quartz reststrahlen plates was replaced by it in such a way that there was reflection from the outer and inner surfaces of the window. The cell was connected to a vacuum pump and

[6] R. G. Dickinson and S. Stewart West, Phys. Rev. **35,** 1126 (1930).

[7] R. W. Wood, Physical Optics, p. 429 (1929).

a tank of SO_2 by a three way stopcock so that it might be alternately evacuated and filled with SO_2 at a pressure of two atmospheres. No change, whatever, in the galvanometer was observed when the cell was emptied and filled with SO_2. This seems to show that this gas does not reflect at either 8.7μ or 20.75μ.

The results of Table II are in agreement with results of Rubens and von Wartenberg[8] for the 22.9μ reststrahlen with the exception of CS_2. For this gas, using a cell about 8″ long, these authors get a value of 97.8 percent as compared with my value of 86 percent for a 4″ cell.

Coblentz[9] observes absorption bands at or near 6.7μ for liquid $CHCl_3$ (0.16 mm layer) and CCl_4 (0.1 mm layer) which are not observed for the vapor with the 6.7μ reststrahlen.

For CCl_4 there is a Raman line corresponding to an active infrared vibration at a wave-length of 31.6μ and for $CHCl_3$ there is a line corresponding to 27.93μ. Also for $(C_2H_5)_2O$ there is a line corresponding to a wave-length at 23μ. There is no corresponding absorption for the $CHCl_3$ line but the low transmission of ether at 22.9μ and CCl_4 at 32.8μ may be associated with the Raman indications.

Optical properties of various substances. Lacquer films may be prepared by dropping a single drop of colorless brushing lacquer on a large water surface. The lacquer spreads out immediately and the amyl acetate evaporates leaving a tenacious film. These films are useful as windows for absorption cells and so their optical properties are of interest. Since the films are of the order of 1μ thickness, there is no total reflection on account of the destructive interference between the energy reflected from the front and back surfaces. The absorption of a typical film is given in the first row of Table III. These films are so transparent that the reststrahlen are not seriously weakened in passing twice through four films, besides the sooted film over the first hole in the reststrahlen apparatus and the film over the Welschback mantle chimney. Values for a film covered with soot are also given in Table III.

TABLE III. *Percent transmission.*

Material	Description	6.7μ	8.7μ	20.75μ	22.9μ	27.3μ	29.4μ	32.8μ
Lacquer film	Thickness of order of wave-length of visible light	96	93	97	98	99	99	100
Mica	10μ thickness	83	22	19	00	35	42	44
Soot on Lacquer film	Opaque to visible	25	22	67	53	60	67	60
Amorphus quartz	10μ thickness	86	02	01	03	51	55	68
Glass	3μ thickness	93	07	12	14	48	51	56
Cellophane	25μ thickness Cigarette wrapping	33	04	04	01	20	25	26
MgO	Deposit of fumes from burning Mg ribbon	88	86	04	02	90	93	87
ZnO	Deposit of fumes from Zn arc	99	80	15	05	93	79	80

[8] H. Rubens and H. von Wartenberg, Verh. d. D. Phys. Ges. **13,** 796 (1911).

[9] W. W. Coblentz, Investigations of infrared spectra, part I pp. 180 and 182.

Other possibilities for windows in this region are mica, quartz, glass and cellophane. Their transmissions are given in Table III.

In a MgO deposit, we have an interesting absorption at 22.9μ. It seemed from the results given in Table III that one might expect a reststrahlen for MgO near 23μ. The Vitrofrax Corporation of Los Angeles supplied the author with some beautiful synthetic crystals of β-MgO with which experiments were made. There is no doubt but that this material showed a strong reststrahlen near 23μ as will be observed from its reflectivity given in Table IV.

TABLE IV. *Percent reflection*

Description of reflector		22.9μ	32.8μ
Deposit of MgO from burning Mg ribbon		0	0
Reflection $\beta-$MgO		80	33
Galena		28	24
Stibinite		>16	—
Mica		32	—
Paraffin		04	—
Pencil mark on paper		09	—
Silver covered with	Soot coating	43	48
	MgO coating	08	91
	ZnO coating	01	52
	Optical black	31	—
Gold foil blackened with bismuth		>19	—
KBr		04.3	—
KI		05.5	—
KBr+1.5μ CaF_2 deposited by evaporation		10	—
KI+1.5μ CaF_2 deposited by evaporation		13	—

It was not convenient to measure the reflectivity of β-MgO for the other wave-lengths but it was possible to substitute the magnesia for one of the reststrahlen plates and determine the relative galvanometer deflections. This gives the ratio of the reflectivity of MgO to that of the reststrahlen plate. Assuming 0.7 for the reflectivity of the reststrahlen plates we get the approximate values for the reflectivity which are given in Table V.

TABLE V. *Percent reflection of $\beta=MgO$.*

6.7μ	8.7μ	20.75μ	22.9μ	27.3μ	29.4μ	32.8μ
5	10	49	80	42	35	33

S. Tolksdorf[10] reported the fundamental for MgO at 14.2μ but since MgO has a cubic lattice and therefore only one reststrahlen, it does not seem possible that the 14.2μ absorption that he reports can be the fundamental. This point requires further investigation.

S. Tolksdorf predicts, from the absorption spectrum of ZnO, that this material has fundamental absorption bands at 22 and 28μ. The data in Table III give an absorption for one and not the other of these bands. An investigation of the reflectivity of zincite is being made to clear up these points.

Measurements on a KI crystal would indicate that a layer of this material 2 cm in thickness would transmit 50 percent of the 32.8μ reststrahlen.

[10] S. Tolksdorf, Zeits. f. phys. Chem. **132,** 161 (1928).

ON THE AXIAL ROTATION AND SPECTRA OF STARS

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Abstract

Struve's remarkable relation between high observed axial rotations of stars and their bright line spectra is considered theoretically. It is shown that the two phenomena are closely related to the same electromagnetic effects that account for the anomalous solar rotation. High electromagnetic winds, resulting from crossed electric and magnetic fields, account for the high apparent rotational velocity and transfer sufficient momentum to the star in the course of stellar time to account for the high true rotations necessary to produce fission. The large electromagnetic wind velocities require the presence of comparatively large radial electric fields and it is shown that these can add sufficient additional excitation energy to the atmospheric ions to produce bright line spectra. Thus, high apparent axial rotations, high true rotations and bright line spectra in stars are intimately related and the existence of one, usually demands the presence of the others. An approximate expression is derived for the time rate of increase of angular momentum in a star.

IN TWO recent papers,[1] Otto Struve has drawn attention to a remarkable correlation between the spectra of stars and their apparent rotation as derived from measurements of Doppler displacements. Dr. Struve points out that emission lines are found principally in the O and B type stars and that in these "Excessive rotations, estimated at . . . (. . . 250 km/sec or more), are frequent. Apparently bright lines occur preferentially in stars having rapid axial rotation." The very high peripheral velocities indicated by his observational data suggest that certain stars are rotating so fast that they are on the verge of division to form binary systems. This conclusion is in accord with statistical data on binary systems which show that most close binary systems are B type stars or later. In the following discussion we will assume that the internal constitution and atmosphere of a given star is not greatly different from that of our sun and show that Dr. Struve's strange observed relations follow directly from a consideration of electromagnetic effects which we have shown to account for certain observed solar peculiarities.

Superposed Electromagnetic Winds

In a series of papers dealing with the electricity and magnetism of the sun[2] it has been shown that the observed variations of the apparent solar rotation with latitude, altitude, and time are readily explained in terms of atmospheric motions superposed upon the body rotation of the sun proper. These systematic motions of the atmosphere result from the interaction of

[1] O. Struve, Astrophys. J. **72,** 1 (1930); **73,** 94 (1931).

[2] R. Gunn, Phys. Rev. **35,** 635 (1930); **36,** 1251 (1930); **37,** 283 (1931); **37,** 983 (1931); **37,** 1129 (1931).

crossed electric and magnetic fields with the atmospheric ions and we may express its magnitude u by[2]

$$u = \frac{E \times B}{B^2(1 + (R/\lambda)^2)} \tag{1}$$

where E is the radial electric field of the star at the observed level and B is the magnetic field (both quantities being expressed in e.m.u.), R the radius of the spiral generated by the moving ion, and λ the mean free path. We will hereafter refer to this systematic superposed atmospheric motion of the ions as an "electromagnetic wind."

The electrical energy dissipated in the solar atmosphere is an appreciable fraction of the total radiated energy.[2] This seems probably to be true in all stars having magnetic fields and indicates that stars with high surface temperatures (high radiation per unit area) are surrounded by a comparatively large radial electric field. Thus in O and B type stars with surface temperatures ranging from 35,000° to 12,000° electrical effects would be expected to be very important. We have no knowledge of the magnetic field of a star and can only suggest that its magnitude and distribution is not unlike that of the sun. If this is the true situation then we would expect the ratio of the magnitudes of the electric and magnetic fields in early type stars to be large and high velocity electromagnetic winds to result. Dr. Struve's observation that excessive rotations are common in O and B type stars is consistent with the above conclusions.

Excitation of Radiation by Electric Fields

Eddington[3] has concluded that bright line spectra in a non-nebulous star is evidence for the existence of "thunderstorms" in the atmosphere of the star, but he was unable to make his suggestion quantitative. We proceed to calculate the electrical energy added to an ion during its free path as a result of the presence of an electric field. An ion in the atmosphere of a star having electric and magnetic fields does not move in the direction of the electric field, on the average, but describes a cycloidal path and progresses in a direction at right angles to both the impressed electric and magnetic fields.[2] Due to the presence of the magnetic field, an ion cannot acquire more than a definite amount of energy from the electric field, even if the ion describes an infinitely long free path. The mean energy W added to an ion by the electric field is given by[2]

$$W = mvu[1 + u^2/v^2]^{1/2} \tag{2}$$

while the maximum energy W_m is considerably more than twice as much or

$$W_m = 2mvu(1 + u/v) \tag{3}$$

where m is the mass of the ion, v the component of its initial velocity in a plane perpendicular to B the magnetic field and u the magnitude of the elec-

[3] Internal Constitution of the Stars, (1926).

tromagnetic wind given by Eq. (1). If we neglect the relatively less frequent case of successive collisions where an ion of initially large energy collides with another and starts it off with abnormally high velocity, we can express Eq. (2) in terms of the electromagnetic wind velocity u and the surface temperature of the star. Thus if we express W in terms of equivalent electron volts V, Eq. (3) becomes

$$V = \frac{u(2mkT)^{1/2}}{10^8 e}\left[1 + \frac{u^2 m}{2kT}\right]^{1/2} \tag{4}$$

where e is the electronic charge expressed in e.m.u., k the Boltzmann constant, and T the atmospheric or effective surface temperature. Table I gives the average increase in energy of an ion due to electrical fields in terms of equivalent electron volts, assuming that the initial energy of the ion when it starts its path is purely thermal. Many of the ions and electrons will have more than these energies and can produce additional excitation.

It will not be necessary to discuss in detail the exact mechanism whereby bright emission lines are produced, for it should be clear from Table I that ions in the atmosphere of a star can absorb sufficient energy from the star's electric field to excite bright line radiation. The table and Eq. (2) bring out

TABLE I. *Average increase in energy due to electric field.*

	Hydrogen ion Surface Temperature		Electron Surface Temperature	
u km/sec	10,000°	20,000°	10,000°	20,000°
10	1.74 volts	2.19 volts	0.031 volts	0.044 volts
25	7.80 "	8.46 "	0.079 "	0.111 "
50	28.8 "	29.4 "	0.16 "	0.22 "
100	112. "	113. "	0.32 "	0.45 "

clearly that the electrical excitation energy and hence the prevalence of bright lines increases rapidly with increase in the magnitude of the electromagnetic wind which is proportional to the apparent rotational velocity. Thus the theory that has been developed to account for the observed anomalies of the sun's rotation leads directly to a quantitative explanation of Struve's observed relation between high rotational velocities and bright line spectra in stars.

ADDED ANGULAR MOMENTUM AND BODY ROTATION

With the possible exception of close binary stars in which the axial and orbital periods are identical, it seems impossible to determine the true rotational period of a star, either by observing the motion of its magnetic pole or by a determination of its departure from a true spherical form. We must have knowledge of the true body rotation in order to separate the various components of the motion and we are forced to assume that the initial rotation of a star is small and estimate the body rotation from the observed apparent motions, the physical properties of its atmosphere and its age. The directions of the electric and magnetic fields of stars are undoubtedly related to the

direction of their rotation in the same manner as those of the sun and earth. The electromagnetic winds therefore blow in the direction of the body rotation, but much faster, and add momentum to the star proper. Thus, we definitely abandon the principle of the conservation of momentum in an evolving star. In connection with the sun this effect was considered[2] and it was shown that since the sun was formed, sufficient angular momentum has been transferred to the sun proper by its own electromagnetic winds to account for its present axial rotation.

The superposed systematic momentum of an ion in a star's atmosphere is derived entirely from the radial electric field, and the magnetic field serves only to change the direction of the moving ion. The mechanism is therefore one for converting radial momentum into angular momentum. There can be no reacting momentum transferred to the star's magnetic field by the mechanism described, for the magnetic force on an ion is always at right angles to its motion and the magnetic field cannot transfer energy to the ion or the ion energy to the magnetic field. Momentum, therefore, cannot be transferred by this means and we are left to consider only the momentum transferred to a star by viscous forces between the star proper and its fast moving atmosphere. This transfer of momentum is always in such a direction as to accelerate the axial rotation and calculations indicate that in the course of stellar time the added momentum is adequate to increase the angular velocity until a star becomes rotationally unstable.

The data available for a typical star are not sufficiently complete to warrant a detailed calculation and in the following we shall make a rough calculation which will serve to indicate only the approximate magnitude of the effects. The electromagnetic winds of the star's atmosphere transfer momentum to the star proper which we assume to be a semi-rigid gaseous body held together by gravitational, radiative, and electromagnetic forces. The torque T applied to the star as a result of the systematic motion of its atmosphere is

$$T = \eta A R_0 \frac{du}{dr} = \frac{d\Omega}{dt} \tag{5}$$

where η is the mean coefficient of viscosity of the transition layer between the atmosphere moving with a velocity u and the surface proper, A the effective areas in contact, R_0 the radius of the star, du/dr the radial velocity gradient and $d\Omega/dt$ the time rate of increase of angular momentum. It is clear from Eq. (1) that the superposed electromagnetic wind velocity u drops rather abruptly when the ion pressure increases sufficiently to make the mean free path λ as small as R, the radius of the spiral generated by the ion moving in the magnetic field. If the low lying regions of the star's atmosphere are in gravitational equilibrium, then the difference in altitude Δr, corresponding to a fractional change in the ion pressure of unity, is given by

$$\Delta r = \frac{kT}{zhg} \tag{6}$$

where k is the Boltzmann constant, T the temperature of the atmosphere, z its mean atomic weight, h the mass of a hydrogen atom, and g the surface acceleration due to gravity. The fractional change in the superposed velocity u in the interval given by Δr is also approximately unity so that we may write

$$\frac{\Delta u}{\Delta r} = \frac{zh\gamma M u_0}{kTR_0^2} \tag{7}$$

where u_0 is the superposed electromagnetic wind velocity in the observed regions of the star's atmosphere, γ the gravitational constant and M the mass of the star.

The coefficient of viscosity η of the transition layer is

$$\eta = \frac{(3zhkT)^{1/2}}{2^{3/2}\pi\sigma^2} \tag{8}$$

where σ is the diameter of the gaseous ions or molecules according to kinetic theory. We assume that the effective area in contact is a ring around the equator of the star of width R_0. Combining the foregoing relations and making obvious substitutions we have that the rate of increase in the angular momentum of the star proper is

$$\frac{d\Omega}{dt} = \left(\frac{3zh}{2kT}\right)^{1/2} \frac{zh\gamma u_0 R_0 M}{\sigma^2} \tag{9}$$

or if ω_t is the present value of the angular velocity

$$\omega_t = \omega_0 + \left(\frac{3zh}{2kT}\right)^{1/2} \frac{zh\gamma R_0 u_0 \tau}{\sigma^2 d^2} \tag{10}$$

where ω_0 is the initial angular velocity of the star and will be set equal to zero, d is the radius of gyration of the star about its axis of spin and τ is the age of the star. We have assumed a steady state and have made no attempt to allow for greater values of u_0 during the youth of the star or for its variation with latitude.

Now if V_0 is the apparent or observed peripheral velocity of the star and $\omega_t R_0$ the peripheral velocity of the surface proper then $V_0 = u_0 + \omega_t R_0$ and

$$\frac{V_0}{u_0} = \left[1 + \left(\frac{3zh}{2kT}\right)^{1/2} \frac{zh\gamma R_0^2 \tau}{\sigma^2 d^2}\right]. \tag{11}$$

Numerical data for calculating V_0/u_0 from Eq. (11) are lacking and we must assume that the star is of uniform density, its atmosphere is not unlike that of the sun and its age approximates 2×10^{20} sec. or the mean indicated age of all stars. Substituting therefore $z=3.3$; $h=1.67\times10^{-24}$ gm; $k=1.37\times10^{-16}$; $\sigma=10^{-8}$ cm; $\gamma=6.67\times10^{-8}$; $\tau=2\times10^{20}$ sec; $d^2=0.4R_0^2$ and for a typical B type star $T=15{,}000°$ we find $V_0/u_0=4.1$ and therefore the true rotational velocity is roughly 3/4 the apparent observed value. A similar calculation for the sun yields 6.2 while the observed ratio is 4.0. It is clear from the results of

our calculation that, unless B type stars are much younger in actual years of existence than their state of evolution indicates the true rotations are large fractions of the apparent rotations and therefore many of these types of stars are on the verge of division to form binary systems. It seems clear that high electromagnetic winds necessarily produce high speed axial rotations in a star of moderate age and the calculations of the present paper are not in disagreement with Dr. Struve's conclusion that many B type stars are almost rotationally unstable.

The observed high apparent axial rotations in O and B type stars, together with the well established fact that close binary systems with few exceptions are B type stars or later, seem significant, and strongly suggest that stars in this period of their evolution divide as a result of a tremendous increase in their angular momentum. The increase in angular velocity appears to be accounted for by electromagnetic effects rather than by an increase due to contraction of the star. The contraction of the star may play an important part; but there is great difficulty in accounting for the original angular momentum, and a mechanism to add momentum to the system must be provided somewhere in the plan of stellar evolution. It seems quite possible that the above mechanism for adding angular momentum to a star represents physical reality but further supporting evidence is desirable.

Conclusion

Dr. Struve's values for the apparent peripheral velocity of type B stars (approximating 250 km/sec) together with the present calculations suggest that the electromagnetic winds may have velocities of 50 km/sec or more and therefore in these stars the ratio of the magnitude of the electric and magnetic fields must be very large. The large electric fields are capable of adding considerable energy to the ions constituting the star's atmosphere and emission lines should be observed. The very high superposed atmospheric motion of the star will, as well, transfer momentum to the star proper and we should expect this stage of development of a star to be characterized by a large increase in angular momentum resulting ultimately in the formation of binary systems. Statistical evidence supports this conclusion. We see therefore that high apparent axial rotations, high true rotations and bright line spectra in stars are intimately related and the existence of one usually demands the presence of the others.

THE NEUTRON

By R. M. Langer and N. Rosen
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Abstract

The writers point out that the postulation of the existence of the "neutron," a combination of an electron and a proton, of small size and low energy would be very useful in explaining a number of atomic and cosmic phenomena. They find that a mathematical treatment based on existing theory leads to indications of such a state but no definite proof.

I. Introduction

IT IS an attractive speculation to try to describe a process by which the various elements could be formed. In the present state of atomic theory it is really an anomaly that there are elements other than hydrogen; for no one has hitherto attempted to show that quantum systems could exist with the dimensions and energies appropriate to nuclei or constituents of nuclei. Our purpose here is to indicate how such systems may exist on the basis of wave-mechanics, and thus offer a way of describing the process of building up of the heavier elements.

The present article is devoted to a discussion of a combination of an electron and a proton of low energy and very small size which we shall speak of as the "neutron." Such a particle, if it exists, must have a mass but slightly smaller than that of a hydrogen, a diameter of 10^{-12} to 10^{-15} cm, and energy of the order of magnitude of m_0c^2 ($15m_0c^2$ is an upper limit; m_0 = electron mass) less than that of hydrogen in order to account for observed phenomena. It seems proper to begin by pointing out reasons for the assumption of the existence of a neutron and to show how it might help to explain certain phenomena.

II. Applications

In most ordinary phenomena the effect of a particle like the neutron would be unobservable. It is small enough, for example, to penetrate material walls and therefore would not contribute to a gas pressure. Its only large scale property is its gravitational field. In atomic and cosmic processes however, it can play an important role.

1. The process of the increase of atomic number.

In a universe whose initial state was a mass of free protons and electrons it is natural to imagine that the most readily formed combination would be that of ordinary hydrogen. This process has a large cross-section because the final state is comparatively large and because there is attraction at large distances with the possibility of radiation always present to provide for the con-

servation of energy in the change of state involved. On the other hand, a stable combination of two protons or two electrons would surely have to be of extremely small size because we know that down to very small separations the forces are repulsive. The latter fact decreases the probability of close collisions; and any radiation that might occur could only make the collision less intimate. The alternative process of simultaneous collision of at least six particles to form a complex nucleus is obviously unimportant even at high densities, as long as a suitable building process can be described which involves the collision of only two bodies at a time.

Once hydrogen atoms are formed the way is now open for the building up process. The neutron as we describe it, is actually a low state of hydrogen so that in any hydrogen atom there is always a probability of transition into a neutron with emission of a high energy quantum. Due to its small size the neutron has a very small external electric field so that its long range influence is the gravitational attraction. At small distances there are of course further polarization attractions and possibly magnetic effects. Such systems will collide readily in spite of their small size because they are electrically neutral. Resonance, polarization or magnetic forces may then hold them together until a complex system is formed which by expulsion of some of its electrons might rearrange itself into a stable atomic nucleus. A neutron being small and field-free could penetrate outer shells of electrons and enter nuclei. The tremendous initial velocity which must be assumed in the usual picture in which protons or α-particles are added to one element to form a heavier one, is no longer required. The resulting configuration could well be a stable one but need not be the most stable. The measured values of packing fractions indicate a remarkable degree of stability in the ordinary nuclei. It may therefore be that a close cluster of neutrons could lose energy by the expulsion of electrons to form nuclei.

2. Cosmic radiation.

There are two ways of distributing the energy which is released in the formation of helium. Either most of the energy is given out in the formation of neutrons from hydrogen and a smaller amount accompanies the rearrangement of the four neutrons into helium or else the formation of neutrons liberates a comparatively small amount, the remainder of the packing energy being radiated in a single quantum as the rearrangement occurs. In either case the radiation might be of the type of cosmic radiation as observed by Millikan and others. The second alternative however is entirely in agreement with the conclusion of Millikan as to the significance of his measurements. However, the gradual gathering of neutrons with a subsequent sudden transition to a stable nucleus is much more agreeable than the assumption of a multiple collision by means of which this process is ordinarily supposed to happen.

3. High density matter in stars.

The usual explanation of the white dwarfs involving a high degree of ionization of the atoms is not the only one. There are in fact great advantages

from this point of view in favor of our neutron. Being small it has a great mean free path and is comparatively insensitive to light pressure. It therefore goes easily to the center of a gravitating mass. Being neutral and having an extremely small external field, it permits high densities to build up before it deviates appreciably from perfect gas behavior. Further, the possibility of high densities is not dependent on having a high temperature or pressure nor is there much danger of violating the Pauli exclusion principle by exceeding the maximum electron density for a given pressure.

III. Theoretical Treatment

If one naively examines the solutions of the ordinary Schrödinger equation for hydrogen, one is inclined to wonder why, in addition to the ordinary states for quantum numbers, $n=1, 2, 3, \cdots$, there is no state for $n=0$. Since in general the solutions (for $l=0$) are of the form:

$$\psi \sim e^{-r/n} P_n(r)$$

the wave function for this state, if normalized, would be a δ-function, zero everywhere except at the origin, so that this state would correspond to an electron which had fallen into the nucleus. Such a condition in view of the attraction between the two is by no means inconceivable.

That this is unsatisfactory is at once evident. In the first place the energy, which is given by:

$$W = Rh/n^2$$

would be infinite. In the second place, a simple calculation shows that the transition probability from a higher state to this one is zero in every case. From a physical point of view the state can therefore be considered as nonexistent.

However, the above considerations are too rough. The assumption of a $1/r$ potential must certainly be incorrect for small distances (for the infinity at the origin surely does not exist in nature). If then the potential deviates from $1/r$ at small distances, it may well be that an atomic state exists corresponding to the one under discussion with low *but finite* energy, of small *but not zero* dimensions, and therefore with small *but non-vanishing* transition probabilities.

As a better approximation one can consider the electron in a Coulomb field modified by a small correction term, for example, of the form b/r^2 (the singularity still remains however). One can think of this as an actual potential, or one can consider the relativistic Schrödinger equation for a Coulomb field, thus bringing in a b/r^2 term.

If that is done, it is found without difficulty that for s-states ($l=0$), in addition to the usual solutions, there exist solutions corresponding to the second root of the indicial equation with energies given by

$$E_2 = m_0c^2\left[1 + \alpha^2/(n_r + \tfrac{1}{2} - (\tfrac{1}{4} - \alpha^2)^{1/2})^2\right]^{-1/2},$$

where α is the Sommerfeld fine-structure constant. These energies differ very little from the ordinary energies given by:

$$E_1 = m_0c^2\left[1 + \alpha^2/(n_r + \tfrac{1}{2} + (\tfrac{1}{4} - \alpha^2)^{1/2})^2\right]^{-1/2}$$

for the next smaller value of n_r except in the case $n_r = 0$. For this case E_2 is very low:

$$E_2 \sim 0.073 m_0c^2.$$

That is E_2 is nearly m_0c^2 below the energy of a normal hydrogen atom.

The wave functions corresponding to E_2 have singularities for $r = 0$. They are quadratically integrable and hence would be acceptable according to the views of many physicists. However, the variational integrals turn out to be infinite and for this reason we reject them.[1] Incidentally these wave functions are not necessarily orthogonal to the usual ones of energy E_1.

Another way of attacking the problem is to construct potential energy curves which differ inappreciably from e^2/r for distances greater than 10^{-12} cm, but which have much steeper slopes in the range 10^{-12} to 10^{-16} cm and then flatten out and remain finite at the origin. With such potential functions one can obtain a low "neutron" state without appreciably changing the energies of the higher hydrogen levels. However, setting up such a potential function involves several arbitrary factors; and there are as yet no experimental data to determine them without ambiguity. Further development along this line is very intriguing but in their present state of uncertainty the authors feel themselves not bold enough to offer the results for publication.

[1] R. M. Langer and N. Rosen, Phys. Rev. **37**, 658 (1931).

GROUP THEORY AND THE ELECTRIC CIRCUIT*

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Abstract

Electrical networks consisting of inductances, resistances, and capacitances form a group with the impedance function as an absolute invariant. That is, to a given impedance function there corresponds an infinite number of networks, any one of which can be obtained from any other by a special linear transformation of the instantaneous mesh currents and charges of the network. In this manner one may arrive at the complete infinite set of networks equivalent to a given network of any number of meshes. This is done by writing down the three fundamental quadratic forms of the network. Then a linear affine transformation of the instantaneous mesh currents and charges of the network results in the formation of new quadratic forms, the matrices of the coefficients of which represent a member of the group, i.e., an equivalent network. Instead of performing the substitutions, the three matrix multiplications $C'AC$ are used, one for each quadratic form, where A represents the original matrix, C the transformation matrix, and C' its conjugate. It may be possible to extend this theory to include continuous systems where the quadratic forms become integrals or infinite series and one deals with infinite matrices and infinite transformations.

IN 1904, in an address before the Mathematics section of the International Congress of Arts and Science, Professor James Pierpont said, "The group concept, hardly noticeable at the beginning of the century, has at its close become one of the fundamental and most fruitful notions in the whole range of our science."[1] And now this abstract notion of groups finds application in an important branch of physics—electric circuit theory.

Considerable has been written on electrical networks and the impedance function,[2] but it has hardly been suspected that electrical networks formed a group with the impedance function as an absolute invariant and that it was possible to proceed in a continuous manner from one network to its equivalent network by a linear transformation of the instantaneous mesh currents and charges of the network.

Before proceeding with the general n-mesh network it will be instructive to construct the quadratic forms and the impedance function for the two-mesh network with all three network elements present, shown in Fig. 1.

The elements λ_{12}, ρ_{12} and σ_{12} are the elements common or mutual to meshes 1 and 2. λ_{11}, ρ_{11} and σ_{11} are the *total* parameters of mesh 1, that is, they are, respectively, the total inductance, resistance and elastance of mesh

* This is part of a dissertation presented to the Massachusetts Institute of Technology for the degree of Doctor of Science in 1930.

[1] J. Pierpont, Bulletin of the American Mathematical Society **2**, 144 (1904).

[2] O. Heaviside, Electromagnetic Theory, 1912, and Electrical Papers, 1925; J. R. Carson Electric Circuit Theory and the Operational Calculus, 1926; V. Bush, Operational Circuit Analysis, 1929.

1. Similarly, λ_{22}, ρ_{22} and σ_{22} are the total parameters of mesh 2. The quantities i_1 and i_2 are the *instantaneous mesh* currents, the arrows indicating their directions. Let q_1 and q_2 be the corresponding mesh charges, so that

$$i_1 = dq_1/dt \tag{1}$$

$$i_2 = dq_2/dt. \tag{2}$$

The total *instantaneous* magnetic energy in the complete network is given by

$$\begin{aligned} T &= \tfrac{1}{2}(\lambda_{11} - \lambda_{12})i_1^2 + \tfrac{1}{2}\lambda_{12}(i_1 + i_2)^2 + \tfrac{1}{2}(\lambda_{22} - \lambda_{12})i_2^2 \\ &= \tfrac{1}{2}(\lambda_{11}i_1^2 + 2\lambda_{12}i_1i_2 + \lambda_{22}i_2^2). \end{aligned} \tag{3}$$

Similarly, the total *instantaneous* electrostatic energy in the complete network is given by

$$\begin{aligned} V &= \tfrac{1}{2}(\sigma_{11} - \sigma_{12})q_1^2 + \tfrac{1}{2}\sigma_{12}(q_1 + q_2)^2 + \tfrac{1}{2}(\sigma_{22} - \sigma_{12})q_2^2 \\ &= \tfrac{1}{2}(\sigma_{11}q_1^2 + 2\sigma_{12}q_1q_2 + \sigma_{22}q_2^2). \end{aligned} \tag{4}$$

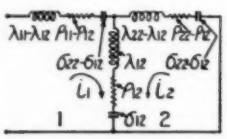


Fig. 1. General two-mesh network.

Finally, the total *instantaneous* power lost in the resistances of the complete network is given by

$$\begin{aligned} R &= (\rho_{11} - \rho_{12})i_1^2 + \rho_{12}(i_1 + i_2)^2 + (\rho_{22} - \rho_{12})i_2^2 \\ &= \rho_{11}i_1^2 + 2\rho_{12}i_1i_2 + \rho_{22}i_2^2. \end{aligned} \tag{5}$$

In more compact notation, T, V and R may, respectively, be written

$$T = \tfrac{1}{2}\Sigma_{jk=1}^{2}\lambda_{jk}i_ji_k \tag{6}$$

$$V = \tfrac{1}{2}\Sigma_{jk=1}^{2}\sigma_{jk}q_jq_k \tag{7}$$

$$R = \Sigma_{jk=1}^{2}\rho_{jk}i_ji_k \tag{8}$$

Since $\lambda_{jk}=\lambda_{kj}$, $\sigma_{jk}=\sigma_{kj}$, $\rho_{jk}=\rho_{kj}$ it is readily seen that by giving j and k all possible values from 1 to 2 in any manner, Eqs. (6), (7) and (8) reduce to Eqs. (3), (4), and (5).

It might be well at this point to generalize Eqs. (6), (7) and (8) for n meshes. This is done simply by changing the upper limit of the summation from 2 to n. For n meshes, then, these equations become

$$T = \tfrac{1}{2}\Sigma_1^n\lambda_{jk}i_ji_k \tag{9}$$

$$V = \tfrac{1}{2}\Sigma_1^n\sigma_{jk}q_jq_k \tag{10}$$

$$F = \tfrac{1}{2}\Sigma_1^n\rho_{jk}i_ji_k \tag{11}$$

where j and k take on all possible values from 1 to n, in any manner.

The quantities T, V and F are the so-called quadratic forms[3] which are positive and definite. That is, they are positive for all values of the variable i or q, and they are zero when and only when all the variables are zero or when the corresponding parameters are all zero. The positiveness of these forms follows at once from physical considerations since the magnetic energy, the electrostatic energy and the power lost in the resistances of the network are positive quantities, and are zero when and only when all the currents or charges are respectively zero, or when the corresponding parameters are zero. These quadratic forms play an important role in dynamics, and significant results are obtained from their positive and definite character.

It is instructive to point out here that the coefficients of the quadratic forms (6), (7) and (8) may be obtained directly from certain matrices. Thus, the coefficients of the quadratic form (6) are contained in the matrix

$$\begin{Vmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{12} & \lambda_{22} \end{Vmatrix} \tag{12}$$

and the form is obtained at once by writing

$$\lambda_{11} i_1^2 + 2\lambda_{12} i_1 i_2 + \lambda_{22} i_2^2$$

which is, of course, $2T$. Similarly, the coefficients of the forms (7) and (8), respectively, are contained in the matrices

$$\begin{Vmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{12} & \sigma_{22} \end{Vmatrix} \quad \begin{Vmatrix} \rho_{11} & \rho_{12} \\ \rho_{12} & \rho_{22} \end{Vmatrix} \tag{13}$$

Also, in the n-mesh case, the coefficients of the quadratic forms T, V and F are contained, respectively, in the matrices

$$\begin{Vmatrix} \lambda_{11} & \lambda_{12} & \cdots & \lambda_{1n} \\ \lambda_{12} & & & \vdots \\ \vdots & & & \vdots \\ \lambda_{1n} & & \cdots & \lambda_{nn} \end{Vmatrix}, \quad \begin{Vmatrix} \sigma_{11} & \sigma_{12} & \cdots & \sigma_{1n} \\ \sigma_{12} & & & \vdots \\ \vdots & & & \vdots \\ \sigma_{1n} & & \cdots & \sigma_{nn} \end{Vmatrix}, \quad \begin{Vmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1n} \\ \vdots & & & \vdots \\ \vdots & & & \vdots \\ \rho_{1n} & & \cdots & \rho_{nn} \end{Vmatrix} \tag{14}$$

From these matrices, the respective quadratic forms of the n-mesh network as well as the respective networks are readily constructed.

The impedance function is obtained from the determinant of the network.[4] Thus the determinant of the network of Fig. 1 is

$$D_1 = \begin{Vmatrix} \lambda_{11}p + \rho_{11} + \sigma_{11}/p & \lambda_{12}p + \rho_{12} + \sigma_{12}/p \\ \lambda_{12}p + \rho_{12} + \sigma_{12}/p & \lambda_{22}p + \rho_{22} + \sigma_{22}/p \end{Vmatrix} \tag{15}$$

and the impedance function is obtained by dividing this determinant by the minor of the element in the first row and first column. Thus

$$Z(p) = \frac{D_1}{\lambda_{22}p + \rho_{22} + \sigma_{22}/p}. \tag{16}$$

[3] See M. Bôcher, Introduction to Higher Algebra, 1927, p. 150.

[4] V. Bush, reference 2, Chapter III.

It will be helpful first to consider the simple two-mesh network containing only two kinds of network elements shown in *a*, Fig. 2.

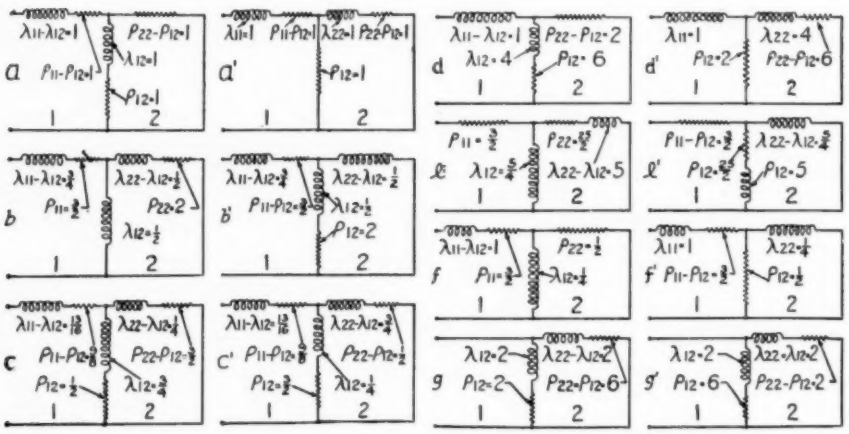
The parameters of the network are $\lambda_{11}=2$, $\lambda_{22}=1$, $\lambda_{12}=1$; $\rho_{11}=2$, $\rho_{22}=2$, $\rho_{12}=1$, and thus the quadratic forms are

$$T = \tfrac{1}{2}(2i_1^2 + 2i_1i_2 + i_2^2) \tag{17a}$$

$$F = \tfrac{1}{2}(2i_1^2 + 2i_1i_2 + 2i_2^2) \tag{17b}$$

and the matrices of the coefficients of these forms are

$$\left\| \begin{matrix} 2 & 1 \\ 1 & 1 \end{matrix} \right\|, \quad \left\| \begin{matrix} 2 & 1 \\ 1 & 2 \end{matrix} \right\|. \tag{18}$$



Some members of the group of networks having $Z(p) = \dfrac{p^2+4p+3}{p+2}$

Fig. 2.

The minimal networks of the impedance function $Z(p) = \dfrac{p^2+4p+3}{p+2}$

Now perform the following linear transformations of the instantaneous mesh currents in the network

$$i_1 = i_1' \tag{19a}$$

$$i_2 = a_{21}i_1' + a_{22}i_2' \tag{19b}$$

where the a's are any real numbers, positive or negative. Substituting these values for i_1 and i_2 in the quadratic forms (17a) and (17b), we have

$$T = \tfrac{1}{2}[(2 + 2a_{21} + a_{21}^2)i_1'^2 + (2a_{22} + 2a_{21}a_{22})i_1'i_2' + (a_{22}^2)i_2'^2] \tag{20a}$$

$$F = \tfrac{1}{2}[(2 + 2a_{21} + 2a_{21}^2)i_1'^2 + (2a_{22} + 4a_{21}a_{22})i_1'i_2' + (2a_{22}^2)i_2'^2] \tag{20b}$$

Thus, the transformations (19) give the new quadratic forms (20). The two matrices containing the coefficients of these new forms are then

$$\left\| \begin{matrix} 2 + 2a_{21} + a_{21}^2 & a_{22} + a_{21}a_{22} \\ a_{22} + a_{21}a_{22} & a_{22}^2 \end{matrix} \right\|, \quad \left\| \begin{matrix} 2 + 2a_{21} + 2a_{21}^2 & a_{22} + 2a_{21}a_{22} \\ a_{22} + 2a_{21}a_{22} & 2a_{22}^2 \end{matrix} \right\| \tag{21}$$

These two matrices determine an infinite group of networks equivalent to the network shown in *a*, Fig. 2. The different networks are obtained by assigning different real values to a_{21} and a_{22}. Thus, for example, by giving the values of $+1$ and -1 respectively to a_{21} and a_{22}, the matrices (21) become under these substitutions

$$\left\| \begin{matrix} \frac{5}{4} & \frac{1}{2} \\ \frac{1}{2} & 1 \end{matrix} \right\|, \quad \left\| \begin{matrix} \frac{3}{2} & 0 \\ 0 & 2 \end{matrix} \right\|. \tag{22}$$

From these matrices the parameters of the network are readily obtained. They are

$$\lambda_{11} = \frac{5}{4}, \quad \lambda_{22} = 1, \quad \lambda_{12} = \frac{1}{2}; \quad \rho_{11} = \frac{3}{2}, \quad \rho_{22} = 2, \quad \rho_{12} = 0$$

and the corresponding network is shown in *b*, Fig. 2. It is a simple matter to verify the fact that the networks *a* and *b* of Fig. 2 have the same impedance function, namely,

$$Z(p) = \frac{p^2 + 4p + 3}{p + 2}. \tag{23}$$

In the same way, by assigning different real values to a_{21} and a_{22}, one can obtain the complete infinite group of networks having (23) for an impedance function. Thus, for example, all the networks shown in Fig. 2 have the same impedance function, namely, (23). These networks are some of the members of the infinite group of networks contained in the tensors (21). It is not difficult to ascertain what values of a_{21} and a_{22} in the transformation matrix will give these networks.

Note that the networks *a'*-*g'* are, respectively, identical with the networks *a*-*g*, except that the branches in mesh 2 are interchanged. The former networks may thus be considered images of the latter. Mathematically, two networks with their branches in mesh 2 interchanged, are considered different networks, and to exhaust the complete infinite group of networks, both networks and their images must be included.

Note also that the networks *d*-*g* and their respective images *d'*-*g'* are minimal networks. That is, they are the networks of the group containing the least number of network elements. These can be easily obtained from the tensors (20). Finally, note that it is unnecessary to go through the work of substituting (19) in (17) to obtain the matrices (21) of the quadratic forms (20). We merely make use of an important theorem on matrices, namely, that if we subject the x's in a quadratic form with matrix A to a linear transformation with matrix C, we obtain a new quadratic form with the matrix $C'AC$, where C' is the conjugate of C.[5] In open form, the matrix of the new quadratic form is obtained by multiplying the three matrices

[5] M. Bôcher, reference 3, Theorem 1, p. 129.

$$\left\| \begin{matrix} c_{11} & c_{21} \cdots c_{n1} \\ c_{12} & \vdots \\ \vdots & \vdots \\ c_{1n} \cdots\cdots & c_{nn} \end{matrix} \right\| \times \left\| \begin{matrix} a_{11} & a_{12} \cdots a_{1n} \\ a_{21} & \vdots \\ \vdots & \vdots \\ a_{n1} \cdots\cdots & a_{nn} \end{matrix} \right\| \times \left\| \begin{matrix} c_{11} & c_{12} \cdots c_{1n} \\ c_{21} & \vdots \\ \vdots & \vdots \\ c_{n1} \cdots\cdots & c_{nn} \end{matrix} \right\|. \tag{24}$$

In our problem, the linear transformation is (19), the matrix of which is

$$\left\| \begin{matrix} 1 & 0 \\ a_{21} & a_{22} \end{matrix} \right\| \tag{25}$$

which corresponds to the C matrix. Hence, using this matrix and the matrices (18), we obtain for the matrices of the transformed quadratic forms

$$\left\| \begin{matrix} 1 & a_{21} \\ 0 & a_{22} \end{matrix} \right\| \times \left\| \begin{matrix} 2 & 1 \\ 1 & 1 \end{matrix} \right\| \times \left\| \begin{matrix} 1 & 0 \\ a_{21} & a_{22} \end{matrix} \right\| \tag{26a}$$

$$\left\| \begin{matrix} 1 & a_{21} \\ 0 & a_{22} \end{matrix} \right\| \times \left\| \begin{matrix} 2 & 1 \\ 1 & 2 \end{matrix} \right\| \times \left\| \begin{matrix} 1 & 0 \\ a_{21} & a_{22} \end{matrix} \right\|. \tag{26b}$$

Performing the multiplication of the matrices in (26a), we have

$$\left\| \begin{matrix} 2 + 2a_{21} + a_{21}^2 & a_{22} + a_{21}a_{22} \\ a_{22} + a_{21}a_{22} & a_{22}^2 \end{matrix} \right\|. \tag{27a}$$

Note that this is the left-hand matrix of (21), which was obtained from the transformed quadratic forms (20). In the same way, performing the matrix multiplication in (26b), we have

$$\left\| \begin{matrix} 2 + 2a_{21} + 2a_{21}^2 & a_{22} + 2a_{21}a_{22} \\ a_{22} + 2a_{21}a_{22} & 2a_{22}^2 \end{matrix} \right\| \tag{27b}$$

which is the right-hand matrix of (21).

Thus, however complicated a network may be, and however numerous its meshes, a transformation (24) will give the complete set of equivalent networks. Some of the networks of this infinite set may contain negative as well as positive elements. To obtain networks with only positive elements, it is necessary that the transformation matrix be such that the elements in the main diagonal of the transformed matrix are positive and greater than the corresponding non-diagonal elements.

The infinite group of networks with all three kinds of network elements, namely, inductance, resistance and capacity elements, which have the same impedance function, are obtained exactly in the same manner. Now, however, the transformations are

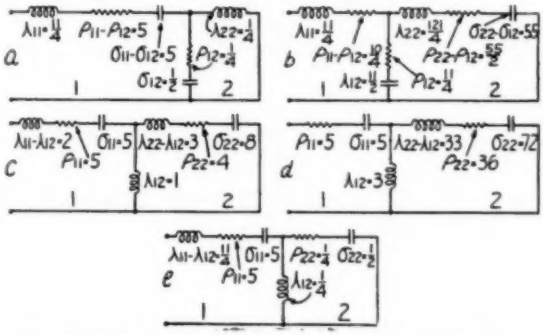
$$i_1 = i_1' \tag{28a}$$

$$\begin{aligned} i_2 &= a_{21}i_1' + a_{22}i_2' \\ q_1 &= q_1' \\ q_2 &= a_{21}q_1' + a_{22}q_2' \end{aligned} \tag{28b}$$

and we will have three matrices representing a network instead of two. Fig. 3 shows some of the members of the group of networks having the impedance function

$$Z(p) = \frac{11p^4 + 32p^3 + 64p^2 + 60p + 40}{p(4p^2 + 4p + 8)}. \tag{29}$$

As before, the number of arbitrary constants, namely a_{21} and a_{22}, tells us the number of network elements which may be eliminated from the network without disturbing the invariance of the impedance function. Thus, for the two-mesh network containing three kinds of elements, the minimal forms will have, in general, seven elements.



Some members of the group of networks having

$$Z(p) = \frac{11p^4 + 32p^3 + 64p^2 + 60p + 40}{p(4p^2 + 4p + 8)}.$$

Fig. 3.

For the general case, then, of networks of any number of meshes containing all three kinds of network elements, namely, inductance, resistance and elastance elements, we have the following three matrices which represent or definitely fix the network.

$$\left\| \begin{matrix} \lambda_{11} & \lambda_{12} \cdots & \lambda_{1n} \\ \lambda_{12} & & \vdots \\ \vdots & & \vdots \\ \lambda_{1n} & \cdots\cdots & \lambda_{nn} \end{matrix} \right\|, \quad \left\| \begin{matrix} \rho_{11} & \rho_{12} \cdots & \rho_{1n} \\ \rho_{12} & & \vdots \\ \vdots & & \vdots \\ \rho_{1n} & \cdots\cdots & \rho_{nn} \end{matrix} \right\|, \quad \left\| \begin{matrix} \sigma_{1n} & \sigma_{12} \cdots & \sigma_{1n} \\ \sigma_{12} & & \vdots \\ \vdots & & \vdots \\ \sigma_{1n} & \cdots\cdots & \sigma_{nn} \end{matrix} \right\| \tag{30}$$

Making the following linear transformations of the instantaneous mesh currents or charges in the network, we have

$$\left.\begin{aligned} i_1 &= i_1' \\ i_2 &= a_{21}i_1' + a_{22}i_2' + \cdots + a_{2n}i_n' \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ i_n &= a_{n1}i_1' + a_{n2}i_2' + \cdots + a_{nn}i_n' \end{aligned}\right\} \tag{31a}$$

for the currents, and

$$\begin{aligned} q_1 &= q_1' \\ q_2 &= a_{21}q_1' + a_{22}q_2' + \cdots a_{2n}q_n' \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ q_n &= a_{n1}q_1' + a_{n2}q_2' + \cdots + a_{nn}q_n' \end{aligned} \tag{31b}$$

for the charges.

The three fundamental forms of the electric network of n meshes, whose coefficients are determined from the three matrices (31), are, respectively,

$$T = \tfrac{1}{2}\Sigma_1^n \lambda_{jk} i_j i_k \tag{32a}$$

$$F = \tfrac{1}{2}\Sigma_1^n \rho_{jk} i_j i_k \tag{32b}$$

$$V = \tfrac{1}{2}\Sigma_1^n \sigma_{jk} q_j q_k. \tag{32c}$$

The substitution of the transformations (31) in (32), results in three new quadratic forms, namely,

$$T' = \tfrac{1}{2}\Sigma_1^n \lambda_{jk}' i_j' i_k' \tag{33a}$$

$$F' = \tfrac{1}{2}\Sigma_1^n \rho_{jk}' i_j' i_k' \tag{33b}$$

$$V' = \tfrac{1}{2}\Sigma_1^n \sigma_{jk}' q_j' q_k'. \tag{33c}$$

The coefficients of these new quadratic forms, λ_{jk}', ρ_{jk}' and σ_{jk}' will of course be functions of the elements of the matrices (30) of the original quadratic forms (32) and of the a coefficients of the transformations (31). This has already been noted in the previous two-mesh example.

The transformation matrix, which contains the coefficients of the transformations (31) may be written

$$C = \begin{Vmatrix} 1 & 0 & \cdots & 0 \\ a_{21} & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ a_{n1} & \cdots & & a_{nn} \end{Vmatrix} \tag{34}$$

The matrices containing the coefficients of the new quadratic forms (33) are of course

$$\begin{Vmatrix} \lambda_{11}' & \cdots & \lambda_{1n}' \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \lambda_{1n}' & \cdots & \lambda_{nn}' \end{Vmatrix}, \quad \begin{Vmatrix} \rho_{11}' & \cdots & \rho_{1n}' \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \rho_{1n}' & \cdots & \rho_{nn}' \end{Vmatrix}, \quad \begin{Vmatrix} \sigma_{11}' & \cdots & \sigma_{1n}' \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \sigma_{1n}' & \cdots & \sigma_{nn}' \end{Vmatrix}. \tag{35}$$

These matrices contain the complete infinite group of networks having for an impedance function the impedance of the network of (30). The impedance function is thus an *absolute* invariant to a linear transformation of the instantaneous currents or charges of the networks in which the indicial current and corresponding charge are kept invariant.[6] The matrices (35) include within them the matrices (30), which are obtained by the *identity* transformation, namely,

[6] See also the Appendix.

$$\begin{aligned} i_1 &= i_1' \\ i_2 &= \quad i_2' \\ i_3 &= \qquad i_3' \\ &\cdots\cdots\cdots \\ i_n &= \qquad\qquad i_n' \end{aligned} \tag{36}$$

The C matrix corresponding to this transformation is the *identity* matrix

$$\begin{Vmatrix} 1 & \cdots & 0 \\ 0 & 1 & \vdots \\ \vdots & & \vdots \\ 0 & \cdots & 1 \end{Vmatrix} \tag{37}$$

As in the two-mesh example, the actual substitution of the transformations (31) in the quadratic forms can be avoided by making use of the transformation theorem (24). Thus, the tensors (35) are obtained from the matrices (30), and the transformation matrix C (34) by the following matrix multiplications:

$$\begin{Vmatrix} 1 & a_{21} & \cdots & a_{n1} \\ 0 & a_{22} & & \vdots \\ \vdots & \vdots & & \vdots \\ 0 & a_{2n} & \cdots & a_{nn} \end{Vmatrix} \times \begin{Vmatrix} \lambda_{11} & \cdots & \lambda_{1n} \\ \vdots & & \vdots \\ \lambda_{1n} & \cdots & \lambda_{nn} \end{Vmatrix} \times \begin{Vmatrix} 1 & 0 & \cdots & 0 \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & & & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{Vmatrix} \tag{38a}$$

$$\begin{Vmatrix} & & & \\ & \text{“} & & \\ & & & \end{Vmatrix} \times \begin{Vmatrix} \rho_{11} & \cdots & \rho_{1n} \\ \vdots & & \vdots \\ \rho_{1n} & \cdots & \rho_{nn} \end{Vmatrix} \times \begin{Vmatrix} & & & \\ & \text{“} & & \\ & & & \end{Vmatrix} \tag{38b}$$

$$\begin{Vmatrix} & & & \\ & \text{“} & & \\ & & & \end{Vmatrix} \times \begin{Vmatrix} \sigma_{11} & \cdots & \sigma_{1n} \\ \vdots & & \vdots \\ \sigma_{1n} & \cdots & \sigma_{nn} \end{Vmatrix} \times \begin{Vmatrix} & & & \\ & \text{“} & & \\ & & & \end{Vmatrix} \tag{38c}$$

The result of the matrix multiplications will be the three tensors (35) where the elements λ', ρ' and σ' are expressed in terms of the elements of the given network, λ, ρ and σ, and the elements a of the transformation matrix C (34).[7]

[7] The expressions for λ', ρ' and σ' in terms of λ, ρ and σ and the elements a of the transformation matrix C may be expressed by the following summations:

$$\lambda_{ik}' = \sum_{r,s=1}^{n} a_{ri} a_{sk} \lambda_{rs}$$

$$\rho_{ik}' = \sum_{r,s=1}^{n} a_{ri} a_{sk} \rho_{rs}$$

$$\sigma_{ik}' = \sum_{r,s=1}^{n} a_{ri} a_{sk} \sigma_{rs}$$

where the summation may be carried out in any order.

I am indebted to Professor E. A. Guillemin for these compact expressions which give the transformed parameters directly in terms of the given parameters and the elements of the transformation matrix.

The above network transformations have been made for the purpose of preserving the invariance of the *driving-point* impedance function. These transformations need not be so limited. Transformations may be made whereby the invariance of the transfer-impedance function is preserved. This gives rise to a new notion of equivalence, namely, equivalence with respect to a *definite mesh*.

It has been noted that the number of arbitrary constants in the transformation matrix determined the number of elements which could be eliminated from the network without disturbing the invariance of the impedance function. Thus, the least number of elements necessary in any network to realize a definite driving-point impedance function, or a definite transfer-impedance function, can be readily determined. This is important because one can tell whether a communication network of any number of meshes has superfluous elements.

Instead of imposing conditions on the a coefficients of the transformation to give minimal networks, it may be possible to obtain equivalence with respect to more than one mesh in a network; that is, to make the instantaneous currents in both the k-mesh and r-mesh, for example, invariant for the complete infinite group of networks. Finally, we may obtain equivalence with respect to, say, j-meshes, by using a still more general transformation.

In the foregoing theory, we have limited ourselves to networks of a finite number of meshes, that is, to networks with n degrees of freedom. There is no reason physically why this theory cannot be applied to networks of an infinite number of meshes, that is, an infinite number of degrees of freedom. Here interesting problems arise which bear intimately on mathematical theory, acoustics, electromagnetic wave theory, elastic waves,—in short, all branches of physics involving oscillations. This is also true for the finite problem, since the theory explained above can be applied to any physical vibrational problem involving a finite number of degrees of freedom, not merely to electric circuit theory. The latter province, however, appears to offer the most fertile soil for further investigation, and to provide a physical picture of the phenomena which occur.

In the problem involving networks with an infinite number of degrees of freedom, we have to deal with matrices and tensors containing an infinite number of elements as well as with quadratic forms which are power series or integrals. The matrices containing the coefficients of the three fundamental quadratic forms will contain an infinite number of elements, as will the transformation matrix and the resulting tensors. But for a physical network of an infinite number of degrees of freedom, we know physically that the total instantaneous magnetic energy, the total instantaneous electrostatic energy and the total instantaneous power lost, are finite quantities. Hence the three fundamental quadratic forms, which are now power series or integrals, are properly convergent. Likewise, the linear transformations, which are linear forms of an infinite number of terms, have meaning, as have the infinite transformation matrices which contain the coefficients of the transformations. Finally, the resulting tensors, which contain an infinite number of elements

have physical meaning. They represent the complete infinite group of networks of an infinite number of degrees of freedom, discrete or continuous systems, which are equivalent in one or all the ways defined above.

The network with an infinite number of degrees of freedom may be merely a continuous system such as the smooth transmission or communication line. Thus, not only may there be an infinite number of different terminal networks which may perform the same function in a communication or transmission system, but also an infinite number of communication or transmission lines, which likewise may perform the same function. That is, there exists an infinite group of lines all of which have the same impedance function.

It will be recalled that this investigation has considered essentially two-terminal networks. By the principle of superposition, it should be possible to extend the theory to networks of any number of terminals. This extension is important, since by means of it any section of a communication network can be removed and replaced by an equivalent section.

In conclusion, it may be useful to suggest problems for further investigation. First, it should be mentioned that the conception that networks form a group in which the impedance is an invariant may prove useful in simplifying many problems in network theory. Thus, for example, the solution for the instantaneous currents of a network of the group at once results in the solutions for the instantaneous currents of all of the infinite number of networks in the group, since these currents are obtained from the former by a simple linear transformation. Furthermore, the solution for the instantaneous currents in one network in the group may be much simpler than for another; and there may be one network in the group for which the computations are least complicated. Hence, if it is necessary to obtain currents and voltages in one network, it may be simpler first to transform the network to an equivalent one, for which the computations are much simpler. This is already recognized, for example, when we transform from Y to Δ and vice versa in three-phase alternating-current network problems. Thus it is probable that simplification may result in operational circuit analysis by the above method.

It should be noted that in the matrix multiplication which gives the tensor containing the complete infinite group of equivalent networks, the impedance function vanishes from the scene. This suggests the possibility that the notion of the impedance function, which is a special creation of the electrical engineer, may perhaps disappear in the future. What we have to deal with are networks, currents and energies; and while the impedance function may be helpful for visualization, it may not be necessary to obtain the final important results.

As has been indicated, the problem of currents and charges in an electrical network is identical with the problem of velocities and displacements in a dynamical system. Although this is generally recognized, there is much in classical dynamic theory that remains to be translated in appropriate language for electric circuit theory. Many questions suggest themselves. What in electric circuit theory corresponds to the principal or normal coordinates in dynamic theory? Is it possible to eliminate the cross product terms in the

fundamental quadratic forms of the electric circuit, thereby giving expressions which are sums of squares of the currents or charges? If it is, can a physical network be built which realizes this?

Problems of networks with an infinite number of degrees of freedom, equivalence with respect to transfer-impedance, equivalence with respect to more than one mesh, networks with more than two terminals—these have been merely intimated. Furthermore, it appears that mathematics does not discriminate against negative network elements, which seems to indicate that perhaps they may be realized physically, though not, of course, by coils, resistors and condensers.

Finally, in the study of an electrical network and its response to an impressed electromotive force, one continually encounters many seemingly unrelated branches of mathematics, such as (1) continued fractions, (2) Cauchy residue theory, (3) asymptotic series, (4) fractional and irrational derivatives and integrals, (5) group theory, (6) Fourier series and transforms, (7) integral equations, etc. It seems almost as if something were there, inarticulately trying to make itself understood. But perhaps it must await a modern Euler.

Acknowledgment

The author wishes to acknowledge his gratitude to Professors E. A. Guillemin and D. J. Struik for their interest and encouragement in the preparation of his thesis of which this paper is a part; to Professor V. Bush for his valuable criticism; and to R. M. Foster for his "A Reactance Theorem"[8] and "Theorems Regarding the Driving-Point Impedance of Two-Mesh Networks";[9] and to W. Cauer for his "Die Verwirklichung von Wechselstromwiderständen vorgeschriebener Frequenzabhängikeit"[10] and "Vierpole."[11]

Appendix

Consider the pair of quadratic forms representing, respectively, the inductance and resistance quadratic forms of an n-mesh network containing inductance and resistance elements:

$$\phi(i_1 \cdots i_n) = \Sigma_1^n \lambda_{jk} i_j i_k \tag{39a}$$

$$\psi(i_1 \cdots i_n) = \Sigma_1^n \rho_{jk} i_j i_k \tag{39b}$$

and form the pencil of quadratic forms

$$\phi p + \psi = \Sigma_1^n (\lambda_{jk} p + \rho_{jk}) i_j i_k. \tag{40}$$

The discriminant of this pencil is the determinant of the network:

$$D(p) = \begin{vmatrix} \lambda_{11}p + \rho_{11} \cdots \lambda_{11}p + \rho_{1n} \\ \lambda_{1n}p + \rho_{1n} \cdots \lambda_{nn}p + \rho_{nn} \end{vmatrix} \tag{41}$$

This is a polynomial which is in general of degree n and may be written

[8] Bell System Technical Journal, vol. 3, 1924,

[9] *Ibid.*

[10] Archiv. für Elektrotechnik, Heft 4, Band 17, 1926.

[11] Elektrischen Nachrichtentechnik, Heft 7, Band 6, 1929.

$$D(p) = \Delta(\lambda)p^n + \Delta(\lambda, \rho)p^{n-1} + \Delta_2(\lambda, \rho)p^{n-2} + \cdots + \Delta_2(\rho,\lambda)p^2 + \Delta_1(\rho,\lambda)p + \Delta(\rho) \quad (42)$$

where $\Delta(\lambda)$ and $\Delta(\rho)$ are the discriminants of ϕ and ψ respectively, while $\Delta_k(\lambda, \rho)$ is the sum of the different determinants which can be formed by replacing k columns of the discriminant of ϕ by the corresponding columns of the discriminant of ψ.

Likewise, form the first minor of $D(p)$, namely,

$$M_{11}(p) = \begin{vmatrix} \lambda_{22}p + \rho_{22} & \cdots & \lambda_{2n}p + \rho_{2n} \\ \vdots & & \vdots \\ \lambda_{2n}p + \rho_{2n} & \cdots & \lambda_{nn}p + \rho_{nn} \end{vmatrix}. \quad (43)$$

This may be written as a polynomial in general of degree $n-1$, namely,

$$M_{11}(p) = M_{11}(\lambda)p^{n-1} + M_{11}^{(1)}(\lambda,\rho)p^{n-2} + \cdots + M_{11}^{(1)}(\rho, \lambda)p + M_{11}(\rho) \quad (44)$$

Now it can be shown that the coefficients $\Delta(\lambda)\cdots\Delta(\lambda, \rho)\cdots\Delta(\rho)$ of $D(p)$ are integral rational invariants of weight two of the pair of quadratic forms ϕ and ψ.[12] Similarly, the coefficients $M_{11}(\lambda)\cdots M_{11}^k(\lambda, \rho)\cdots M_{11}(\rho)$ are integral rational invariants of weight two. Thus it is that the linear transformations of the variables of the quadratic forms make the impedance function $Z(p)$, which is the ratio of $D(p)$ and $M_{11}(p)$; that is, the ratio of two relative invariants of the same weight, an absolute invariant. The foregoing is true also of n-mesh networks containing all three kinds of elements, where we now have in addition to the inductance and resistance quadratic forms, the elastance quadratic form. Thus

$$Z(p) = D(p)/M_{11}(p) \quad (45)$$

becomes under a linear transformation with matrix

$$\begin{Vmatrix} 1 & 0 & \cdots & 0 \\ a_{21} & & \cdots & a_{2n} \\ \vdots & & & \vdots \\ a_{n1} & & \cdots & a_{nn} \end{Vmatrix} \quad (46)$$

$$Z(p) = \frac{\begin{vmatrix} 1 & 0 & \cdots & 0 \\ a_{21} & & \cdots & a_{2n} \\ \vdots & & & \vdots \\ a_{n1} & & \cdots & a_{nn} \end{vmatrix}^2}{\begin{vmatrix} a_{22} & \cdots & a_{2n} \\ \vdots & & \vdots \\ a_{n2} & \cdots & a_{nn} \end{vmatrix}^2} \times \frac{D(p)}{M_{11}(p)} \quad (47)$$

$$= D(p)/M_{11}(p).$$

[12] See M. Bôcher, Introduction to Higher Algebra, 1927, p. 166.

ACCOMMODATION COEFFICIENTS OF POSITIVE IONS OF ARGON, NEON AND HELIUM

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Abstract

Positive ions of argon, neon and helium produced in a low voltage arc were attracted to a spherical metal collector by regulated potentials up to 140 volts. The resulting heating of the collector was measured by a thermal junction and found to be *considerably less* than the product of the current by the attracting voltage. After taking account of the energy scattering at collisions and of the effect of the secondary electron emission, the following values of the "accommodation coefficients" were obtained: argon 0.75 ± 0.05, neon 0.65 ± 0.05 (both between 21 and 141 volts), and helium 0.35 ± 0.05 between 21 and 51 volts and 0.55 ± 0.05 between 111 and 141 volts.

WHEN an attempt was made to measure the amount of energy ϕ_+ delivered to a metal electrode when a positive ion with no kinetic energy is neutralized at its surface,[1] collisions between the ions and neutral molecules within the sheath, and comparatively large electron currents were thought to be the principal factors complicating the calculation and interpretation of the results. By making measurements of the heat generated when positive ions were drawn to the collector by fields so large that practically no electrons could reach the collector, and by working with such low gas pressures that very few ions would make collisions within the sheath it was later believed possible to make these complicating factors negligibly small. Under these conditions, since the positive ions reaching the collector are believed to start at or near the sheath edge with only a negligibly small velocity,[2] ϕ_+ should be easily obtained from the observed heating of the collector at two different negative potentials, if due allowance were made for the kinetic energy of the ions acquired in passing through the sheath. Thus the heating effect H of a current of magnitude j^+ at a given accelerating potential V with respect to the space potential would be

$$H = j^+(V + \phi_+) \tag{1}$$

and the difference between the heating effects at two different accelerating potentials V_f and V_0 would be given by

$$H_f - H_0 = j_f{}^+(V_f + \phi_+) - j_0{}^+(V_0 + \phi_+) \tag{2}$$

whence

[1] Van Voorhis, Phys. Rev. **30**, 318 (1927).
[2] Tonks and Langmuir, Phys. Rev. **34**, 876 (1929).

$$\phi_+ = \frac{(H_f - H_0) - (j_f{}^+V_f - j_0{}^+V_0)}{j_f{}^+ - j_0{}^+}. \tag{3}$$

All of the quantities on the right side of Eq. (3) could then be obtained experimentally by means of our apparatus.

However, the results obtained from the application of this line of reasoning led to the surprising discovery that the heat produced by the positive ions striking a collector and being neutralized at its surface, is *much less* than the equivalent of the kinetic energy which they should acquire from the attracting field. Though this deficiency in heating effect has recently been observed by Found[3] and Güntherschulze,[4] they have ascribed it entirely to the effect which a large secondary electron emission would have upon the apparent and true values of the positive ion currents, and thus have assumed that the effect is only apparent and not real.

Careful measurements over a considerable range of accelerating potentials and gas pressures in argon, neon and helium have led us to conclude that the deficiency in heating effect in these gases is entirely too large to be accounted for by secondary electron emission and consequently at least some of the neutral molecules and metastable atoms formed by the neutralization of the positive ions at a metal surface must have left it with energies much larger than would correspond to the temperature of the metal. This means that positive ions with fairly high velocities may be considered as having accommodation coefficients less than unity just as the gas molecules have at much lower velocities or temperatures.[5]

Some of our measurements have been made under gas pressure conditions such that the effects of collisions of ions with gas molecules within the sheath are no longer negligible; but when these results have been corrected by the use of Runge's[6] theoretical values for the scattering of ion energy by collisions with neutral molecules, they become, in general, fairly consistent with those obtained at the lower gas pressures and may therefore be used in testing collision theories.

Experimental Procedure and Calculation of Results

The observations were taken with apparatus of the same type as was described in detail in the earlier paper.[1] A schematic sketch of the parts in the discharge tube and of the electrical connections is given in Fig. 1. A low voltage arc was maintained between the hot tungsten filament F and the anode A by applying a voltage from the battery B_2, this voltage being from 5 to 10 volts higher than the ionizing potential of the gas in use. The collector C was a metal sphere in which was imbedded a very small copper-constantan

[3] Found, Phys. Rev. **34,** 1625 (1929).

[4] Güntherschulze, Zeits. f. Physik **62,** 600 (1930).

[5] Knudsen, Ann. d. Physik **34,** 593 (1911); **46,** 641 (1915); Soddy and Berry, Proc. Roy. Soc. **84,** 576 (1911); Langmuir, J. Am. Chem. Soc. **37,** 425 (1915); Roberts, Proc. Roy. Soc. **129,** 146 (1930).

[6] Runge, Zeits. f. Physik **61,** 174 (1930).

thermocouple. In the measurements with argon and neon the collector was of molybdenum, 3.1 mm in diameter and with helium it was a 3.0 mm platinum sphere.

The gases were carefully purified by arcs between "misch" metal cathodes and iron anodes in glass reservoirs on the vacuum system, before being admitted to the discharge tube. Observations were made on repeated fillings of a given gas until the results from different fillings were quite reproducible, which condition was taken to indicate that no appreciable impurity was coming from the walls or metal parts of the vacuum tight discharge tube.

Of the quantities on the right side of Eq. (3) j_0^+ and j_f^+ were obtained directly from the readings of the Cambridge Universal Test Set used as A_3 in Fig. 1. To obtain V_0 and V_f it was necessary to find V_s, the space potential

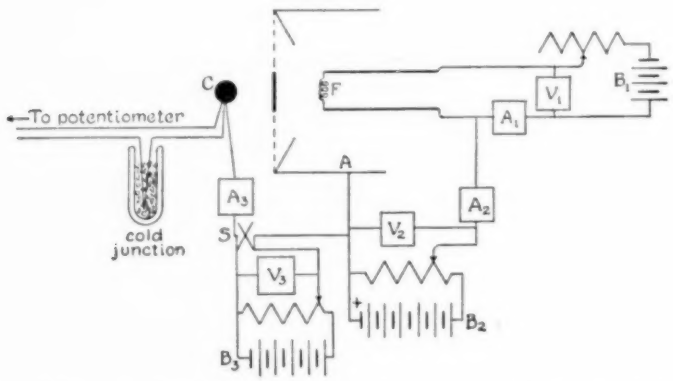

Fig. 1. Schematic sketch of apparatus and arrangement of electrical circuits.

with respect to the anode, by the usual method[7] and add this to the applied potentials as given by V_3 (Fig. 1). The quantity $H_f - H_0$ was obtained from the product of the heat capacity Q of the collecting sphere C and the rate of temperature change dT/dt of C immediately after its potential was changed from V_0 to V_f. Since the temperature, starting at T_0 when $t=0$, approached a final limiting value exponentially,

$$T - T_0 = (T_f - T_0)(1 - e^{-at}) \tag{4}$$

where T was the temperature at time t, e the Naperian base and a a constant dependent upon the existing experimental conditions. Then it follows from (4) that

$$\left(\frac{dT}{dt}\right)_{t=0} = a(T_f - T_0), \text{ where } a = \frac{2.303}{t}\log_{10}\left(\frac{T_f - T_0}{T_f - T}\right) \tag{5}$$

The data for calculating a were obtained by first noting the electromotive force mV_0 of the thermocouple after the potential of the collector had been

[7] Langmuir, Gen. Elec. Rev. **26,** 731 (1923); Science **58,** 290 (1923); Jour. Frank. Inst. **196,** 751 (1923); Langmuir and Mott-Smith, Gen. Elec. Rev. **27,** 449, 538, 616, 762, 810 (1924).

held at V_0 long enough for it to reach a steady temperature. Then simultaneously the collector potential was changed to V_f and two stop watches started. As the temperature of the collector changed, the drum of the potentiometer was slowly turned so as to keep the galvanometer deflection as near zero as possible. At some instant when the deflection was exactly zero one watch was stopped and its time t_1 and the corresponding mV_1 were recorded, after which mV_2 was noted in the same way for time t_2 obtained by means of the second watch. As soon as the temperature became practically constant, which was generally about 5 minutes after t_0, record was made of mV_f. From these data two values of a could be calculated and their mean $\bar{a}$ was used in applying Eq. (5).

In Table I are given typical sets of observations and the resulting quantities obtained from various steps in the calculations. To obtain the tempera-

TABLE I. *Typical sets of observations and calculations for the molybdenum collector in argon at 0.1 mm pressure.*

1	2	3	4	5	6	7	8	9
V_s V_f V_0 Volts	j_0^+ j_f^+ m.a.	t_0 t_1 t_2 sec.	mV_0 mV_1 mV_2 mV_f millivolts	T_f-T_0 T_f-T_1 T_f-T_2 °C	a_1 a_2 $\bar{a}$	Q	MH or $\bar{a}(T_f-T_0)Q$ EH milliwatts	MH/EH
20.0	0.354	0	7.653	25.31				
		19.79	7.945	19.77	0.01248	35.97	11.39	
49.9	.430	36.95	8.149	15.93	.01254			0.786
1.5			9.007		.01251		14.49	
49.8	.432	0	8.990	29.10				
		32.70	9.551	18.80	.01338	36.18	14.06	
81.0	.496	60.80	9.875	12.92	.01336			.751
1.5			10.594		.01337		18.73	
81.0	.498	0	10.582	30.18				
		26.57	11.111	20.80	.01401	36.42	15.32	
110.8	.550	50.11	11.445	14.89	.01385			.740
1.5			12.299		.01393		20.70	

ture differences given in column 5 the corresponding millivolt differences obtained from column 4 were divided by the millivolt differences per degree, of the electromotive force of the thermocouple at the corresponding temperatures. The temperatures and corresponding millivolt differences per degree were readily determined from two curves obtained by plotting against temperature on a large piece of graph paper, the values of mV and $d(mV)/dt$ calculated at 20° intervals from the calibration equation of the thermocouple, $mV_T = 0.0400766T + 0.00004344T^2 - 0.00000002244T^3$.

In column 7 the values of Q are the heat capacities in millijoules per degree for the corresponding mean temperatures. In column 8, MH is the measured heating effect in milliwatts obtained from the observations and calculations, whereas EH is the expected heating on the assumption that all of the kinetic energy gained by the ions from the accelerating field would be delivered to the collector in the form of heat, ϕ_+ being neglected for the present. Thus the value of EH is found from the equation

$$EH = j_f^+(V_f + V_s) - j_0^+(V_0 + V_s). \tag{6}$$

In Tables II, III and IV are given the results obtained in argon, neon and

helium respectively. Column 1 of these tables gives the gas pressure and the assumed positive ion mean free path obtained by taking $2^{1/2}$ times the kinetic theory value for the neutral atoms at the temperature in the discharge tube. In column 2 are given the values of the applied potentials (with respect to the space) after slight adjustment to make the voltage intervals exactly 30 volts, the actual intervals used ranging between 29 and 31 volts since the po-

TABLE II. *Results in argon.*

1	2	3	4	5	6	7	8	9	10	11
					Measured heating / Expected heating			If current varies as sheath area		
P / λ	V	m.a.	S/λ (L&B)	S/λ (R&M)	Unmodified	Corrected		m.a.	*MH/EH*	
						$\phi_+=0$	$\phi_+=V_i-\phi_-$		$\phi_+=0$	$\phi_+=V_i-\phi_-$
0.016 mmHg	20.6	0.106	0.068	same	(0.84^E)	(0.84^E)	(0.76^E)	0.061+		
	50.6	.142	.117	"				.045−	(1.45^E)	(1.31^E)
	80.6	.169	.154	"	.81	.81	.76	.097+	(1.02^F)	(1.96^F)
7.8 mm	110.6	.191	.187	"	.81	.81	.78	.124	($.98^F$)	($.94^F$)
	140.6	.211	.217	"	.80	.80	.78	.146	($.95^F$)	($.92^F$)
								.166		
0.040	20.6	.261	.103	"				.217+		
	50.6	.329	.184	"	.81	.81	.74	.044−	.92	.88
	80.6	.384	.245	"	.80	.80	.76	.285+		
3.15	110.6	.431	.297	"	.77	.77	.74	.340	.88	.84
	140.6	.476	.343	"	.76	.77	.74	.387	.84	.80
								.432	.83	.80
0.10	21.5	.340	.235	"				.277+		
	51.5	.416	.411	.410	.77	.77	.71	.063−	.89	.82
	81.5	.476	.546	.545	.74	.75	.70	.353+		
1.26	111.5	.530	.662	.661	.73	.74	.70	.413	.84	.80
	141.5	.580	.766	.765	.72	.75	.72	.467	.82	.79
								.517	.81	.78
0.25	21.3	.250	.680	.679				.200+		
	51.3	.310	1.20	1.18	.69	.70	.64	.050−	.82	.74
	81.3	.362	1.59	1.55	.68	.71	.66	.260+		
0.505	111.3	.409	1.92	1.87	.68	.77	.73	.312	.80	.75
	141.3	.450	2.20	2.14	.67	.77	.74	.359	.85	.81
								.400	.96	.92
0.50	21.5	.218	1.47	1.44				.172+		
	51.5	.269	2.60	2.53	.69	.77	.70	.046−	1.00	.90
	81.5	.320	3.41	3.32	.64	.78	.72	.223	1.00	.92
0.253	111.5	.373	4.05	3.93	.62	($.87^H$)	($.82^H$)	.274	(1.01^H)	($.94^H$)
	141.5	.424	4.56	4.40	.63	($.92^H$)	($.87^H$)	$.327^I$	(1.00^H)	($.95^H$)
								$.378^I$		

tential change was made by suddenly changing the position of the slider of a slide wire potential divider and the interval could not be exactly duplicated. The values of the measured currents in column 3 are adjusted to correspond to the potentials given in column 2. These adjustments were deemed advisable in order to shorten the calculations involved in the corrections made as explained later, by making it possible to apply these corrections only to the mean values instead of to each individual result which was obtained under

conditions differing only slightly from those of the three to seven other similar results. However, the values of the ratios of the "measured heating" to the "expected heating" given in column 6 are the means of the four to eight

TABLE III. *Results in neon.*

1	2	3	4	5	6	7	8	9	10	11
					Measured heating / Expected heating			If current varies as sheath area		
P / λ	V	m.a.	S/λ (L&B)	S/λ (R&M)	Unmodified	Corrected $\phi_+=0$	Corrected $\phi_+=V_i-\phi_-$	m.a.	MH/EH $\phi_+=0$	MH/EH $\phi_+=V_i-\phi_-$
0.13 mm Hg	22.5	.166c	.314	same	0.64	0.65	0.52	.130+ .036− .180+	0.76	0.61
	52.5	.216	.538	.537	.66	.68	.60	.223	.76	.67
1.68 mm	82.5	.259	.696	.695	.67	.70	.64	.262	.77	.71
	112.5	.298	.830	.828	.68	.72	.67	.296	.78	.73
	142.5	.332	.951	.949						
.30	22.0	.427c	.425	.424	.65	.66	.56	.370+ .057− .470+	.73	.62
	52.0	.527	.738	.736	.66	.68	.61	.553	.73	.66
.752	82.0	.610	.984	.980	.65	.67	.63	.630	.72	.66
	112.0	.687	1.174	1.160	.65	.67	.63	.698	.71	.68
	142.0	.755	1.35	1.33						
.73	21.4	.375	1.08	1.07	.61	.64	.54	.327+ .048 .420+	.71	.59
	51.4	.468	1.90	1.85	.60	.67	.59	.500	.73	.64
.308	81.4	.548	2.51	2.45	.59	($.74^H$)	($.67^H$)	.583	($.79^H$)	($.71^H$)
	111.4	.631	3.00	2.92	.57	($.74^H$)	($.67^H$)	.670	($.78^H$)	($.71^H$)
	141.4	.718	3.38	3.29						

TABLE IV. *Results in helium.*

1	2	3	4	5	6	7	8	9	10	11
					Measured heating / Expected heating			If current varies as sheath area		
P / λ	V	m.a.	S/λ (L&B)	S/λ (R&M)	Unmodified	Corrected $\phi_+=0$	Corrected $\phi_+=V_i-\phi_-$	m.a.	MH/EH $\phi_+=0$	MH/EH $\phi_+=V_i-\phi_-$
.16 mm Hg	21.4	0.0585c	0.616	0.614	0.36	0.38	0.18	Observed positive ion Currents were quite nearly proportional to calculated sheath areas		
	51.4	.0949	.980	.970	.44	.48	.34			
2.18 mm	81.4	.1248	1.24	1.22	.44	.49	.38			
	111.4	.1540	1.44	1.41	.42	.53	.44			
	141.4	.181	1.61	1.57						
.40	21.7	.128c	1.015	1.003	.36	.40	.22	.089+ .039− .139+	.50	.28
	51.7	.178	1.72	1.68	.42	.51	.38	.181	.61	.46
.870	81.7	.220	2.25	2.18	.43	.54	.44	.220	.64	.52
	111.7	.259	2.54	2.47	.42	($.65^H$)	($.57^H$)	.256	($.79^H$)	($.67^H$)
	141.7	.295	3.09	3.00						
1.0	20.9	.182c	2.08	2.01	.37	($.48^H$)	($.25^H$)	.117+ .065− .179+	($.64^H$)	($.34^H$)
	50.9	.244	3.56	3.46	.38	($.58^H$)	($.43^H$)	.232	($.74^H$)	($.55^H$)
.348	80.9	.297	4.48	4.32	.40	($.70^H$)	($.57^H$)	.279	($.88^H$)	($.72^H$)
	110.9	.344	5.37	5.12	.39	($.82^H$)	($.70^H$)	.321	(1.00^H)	($.86^H$)
	140.9	.386	6.46	6.10						

ratios calculated from the actual observations and are not modified in any way.

In columns 4 and 5 are given values of the collision numbers or the ratios of the sheath thickness S to the mean free path λ. The sheath thicknesses used in column 4 were obtained on the assumption of no collisions within the sheath, i.e., by means of Langmuir's equation,[8] and Langmuir and Blodgett's[9] tables, for spherical collectors. The collision numbers in column 5 have been obtained by correcting the sheath thickness for the slowing up of the positive ions by the collisions within the sheath, in accordance with some recent unpublished work of H. P. Robertson and P. M. Morse, assuming that the same fractional shrinkage in thickness takes place in the sheath around the spherical collector as would take place in the sheath of an infinite plane,

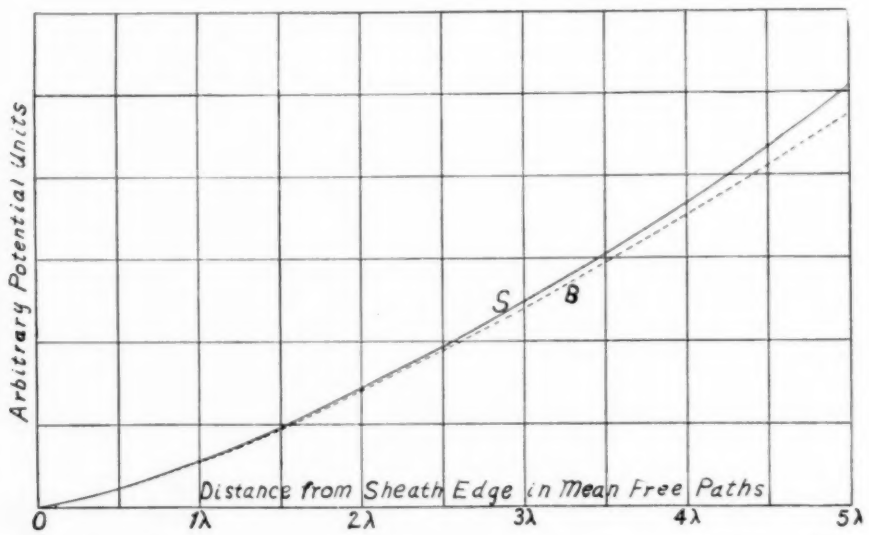

Fig. 2. Potential distribution curves, B from space charge equation (no collisions), and S from assumption of kinetic theory collisions between elastic spheres. For the case of a large plane electrode.

for which case the Robertson and Morse calculations have been made. In Fig. 2[10] the solid line gives the distribution of potential for collision numbers up to five and the dashed line the potential distribution for the same sheath thicknesses if there were no collisions. Thus the difference in abscissas of points having the same ordinate on the two curves gives the shrinkage effect resulting from collisions of ions with neutral molecules within the sheath.

In column 6 are given the mean values of MH/EH obtained in the manner described above in connection with Table I. The values given in column 7 were obtained by correcting for the energy so scattered by collisions of the ions with gas molecules within the sheath that it would not be expected to

[8] Langmuir, Gen. Elec. Rev. **27,** 449 (1924).
[9] Langmuir and Blodgett, Phys. Rev. **24,** 53 (1924).
[10] Published here with the kind permission of Robertson and Morse.

be delivered to the collector. On the assumption of collisions between elastic spheres of equal masses, half of the scattered energy will be delivered to gas molecules on the average, and half will be retained by the ions.[11] All of the energy retained by the ions and part of the energy received by the gas molecules will reach the collector and be delivered in full to it if the accommodation coefficient be unity. However, a part of the energy received by the gas molecules will be so directed as to miss the collector, i.e., if collisions take place at a distance PN, Fig. 3, from the spherical collector no neutral molecules receiving velocities directed at an angle from the normal PN greater

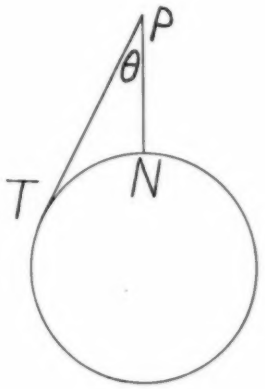

Fig. 3.

than the grazing angle θ will deliver any of their energy to the collector (except as the result of further collisions, and it is assumed that this would just balance the loss of energy from within the grazing angle, resulting from the same cause).

To calculate the fraction of energy, called hereafter $F(E)$, which should not be expected to reach the collector, Runge's[3] theoretical results were used in the following way. Values of $R \sin \theta$ (from Runge's Fig. 3) were plotted as ordinates against θ, R being the energy radius vector and θ the angle with

TABLE V. *Fraction of total energy directed outside of given angles with original direction after from 1 to 5 collisions. (Obtained from Runge's results).*

Angle	Number of collisions				
	1	2	3	4	5
0°	1.000	1.000	1.000	1.000	1.000
10	.941	.968	.973	.980	.988
20	.780	.874	.905	.932	.944
30	.558	.734	.799	.855	.872
40	.346	.569	.688	.752	.781
50	.176	.410	.531	.636	.674
60	.065	.272	.395	.515	.55
70	.015	.164	.278	.396	.45
80	.002	.089	.190	.290	.35
90	.000	.043	.120	.200	.26

[11] Compton and Langmuir, Rev. of Mod. Phys. **2**, 211 (1930); Runge, reference 6.

the direction of the electric field, i.e., with the direction of the energy at the time of the first collision. We then integrated with a planimeter the areas bounded by the zero ordinate, the curves and the 10° interval abscissa lines and from the integrated values found the $F(E)$ directed outside of given grazing angles after from 1 to 5 collisions. The results thus obtained are given in Table V and plotted in Fig. 4, which has also a plot of the grazing angles from points up to 2 mm distant from our 3.1 mm diameter collector.

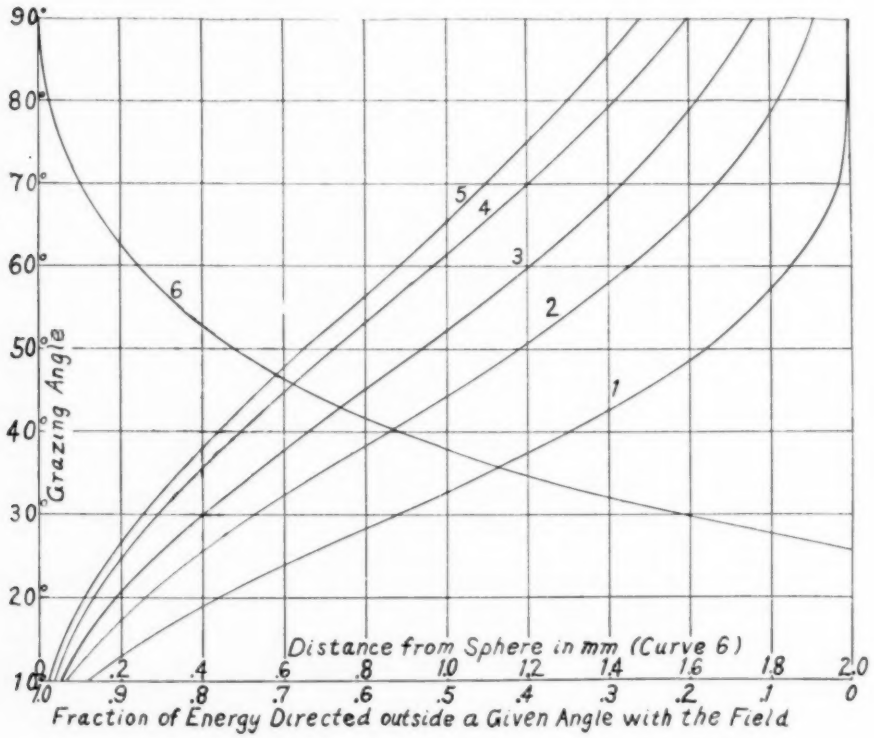

Fig. 4. Curves 1, 2, 3, 4 and 5 show fractions of energy directed outside of given angles with the field direction after from 1 to 5 collisions respectively. Curve 6 is a plot of grazing angle against distance from the 3.1 mm collector.

In applying these results we have followed Runge's assumption that it is legitimate to take account of the scattering of the total energy gained in the whole field between sheath edge and collector by considering piecemeal the energy gained in each λ of distance and the scattering of this energy at subsequent collisions on the way to the collector and then taking the sum of the residual energies at the collector as being the total effective applied potential. Thus, for example, in argon at 0.25 mm pressure (see Table II) with 111.3 volts applied potential the collision number was 1.87 and with 141.3 volts it was 2.14. To calculate the effective potentials (hereafter called EP) it was necessary to obtain from the curves in Fig. 4 the grazing angles recorded in column 2, Table VI, corresponding to the distances from the collector given

in column 1 and the $F(E)$'s directed outside of these grazing angles after collisions, as tabulated in columns 3, 4 and 5 of the same table. Then the potentials with respect to the sheath edge at the various integral λ distances from the collector were obtained from the solid potential distribution curve of Fig. 2, the potentials found being tabulated in columns 6 and 7 of Table IV, whose columns 8 and 9 give the potential differences for the whole λ's and the outside fraction of λ and also, in parentheses, the EP's found by applying the values given in columns 3, 4 and 5 to the potential differences given in 8 and 9 in the following way.

TABLE VI. *Quantities involved in the illustratory example of the calculation of the effective potentials.*

1	2	3	4	5	6	7	8	9
Distance from collector	Grazing angle	Fraction of energy directed outside of grazing angle			Potential relative to sheath edge		Potential difference (Effective P.D.)	
		1 Col.	2 Col.	3 Col.				
0	90.0°	000	.043	.12	141.3	111.3	(129.5)	(104.5)
.14λ	73.2		.137	.25			Total E.P.	
.50λ	59.7	.075					81.1	71.8
.87λ	50.6	.169	.399				(80.4)	(71.2)
1.00λ	48.9	.205	.434		60.2	39.5		39.5
1.14λ	46.8	.224	.457				56.6	(33.3)
1.87λ	38.5	.376				0.0	(46.6)	
2.00λ	37.4	.397			3.6		3.6	
2.14λ	36.2	.422			0.0		(2.5)	

Consider first the potential difference in the first λ distance from the collector. On the assumption that collisions are equally probable all along the path but that all the ions collide once and only once in the distance λ, calculations based on a ten-step division of the first λ for several values of λ, and the resulting potential distributions and energy directions as obtained from the application of the curves in Figs. 2 and 4, showed that the total $F(E)$ received by neutral molecules so directed as to miss the collector is given very accurately by 1/9 the $F(E)$ lost to such molecules at collisions at a point 0.5λ from the collector. Consequently 81.1 $(1-.075/9)$ or 80.4 and 71.8 $(1-0.075/9)$ or 71.2 are the EP differences in the first λ of our examples. For the fractional loss of the energy applied in the second λ, if the $F(E)$ curve for first collision and the potential distribution curve were straight lines we would take 0.5×0.5 the mean of the fractions at λ and 2λ, the one 0.5 factor to give the mean applied potential between λ and 2λ and the other 0.5 factor to take account of the fact that only half of this $F(E)$ is carried by molecules. However, here again ten-step calculations showed that the factor 1/9 should be used instead of 1/8 because of the curvature of the above mentioned curves. For the fractional loss in a given λ of the energy gained outside this λ the fraction $\frac{1}{4}$ was used because the $F(E)$ curves for more than one collision do not differ so greatly from a straight line. Consequently 56.6 $[1-(0.397+0.205)/9]$ $[1-(0.434+0.043)/4]$ or 46.6 was found to be the EP in the second λ of our 141.3 volt case. To obtain the effective part of the potential applied in

the outer fractional λ part of the sheath a slightly different method of calculation was used as will appear from the following examples:

$$3.6\left[1-\frac{0.14}{9}(0.422+0.397)-\frac{0.86}{4}(0.397+0.224)\right]=3.07$$

$$3.07\left(1-\frac{0.457+0.137}{4}\right)\left[1-\frac{0.14}{4}(0.25+0.12)\right]=2.5$$

and

$$39.5\left[1-\frac{0.87}{9}(0.376+0.205)-\frac{0.13}{4}(0.205+0.169)\right]=36.8$$

$$36.8\left[1-\frac{0.87}{4}(0.399+0.043)\right]=33.3$$

Thus the total *EP*'s whose energy may be expected to reach the collector are 129.5 and 104.5 volts instead of the actually applied voltages 141.3 and 111.3 respectively, and the use of the former instead of the latter to calculate the expected heating changed the ratio of *MH* to *EH* from 0.67 to 0.77. By this method of correcting for the amount of energy to be expected to reach the collector all the results tabulated in column 7 of Tables II, III and IV were obtained.

When, instead of using the assumption that $\phi_+=0$, the Schottky[12] assumption that $\phi_+=V_i-\phi_-$, where V_i is the ionizing potential of the gas, is taken into account the results are changed from the values of column 7 to those of column 8 (Tables II, III and IV).

After our experimental tube had been set up and most of the data taken, there came to our attention the work of Oliphant[13] and of Uyterhoeven and Harrington[14] which showed the presence of a fairly large secondary electron emission from negative collectors under conditions somewhat similar to ours. The effect of the secondary electrons would be to make the heating of the collector less than would be expected if all the measured current were carried by positive ions. Since we were not able to measure the secondary emission from the collector directly, although measurements made with an auxiliary Mo plate and Ni collector (added to the discharge tube for this special purpose and not shown in Fig. 1) similar to those used by Uyterhoeven and Harrington[14] showed less than 1 percent secondary emission from the plate under the conditions of our experiments in argon and less than 2 percent in neon (no measurements being made in helium) we have thought it best to show what would be the effect upon our results of secondary electron emissions of about the same magnitude as reported by these investigators. In accordance with Found's suggestion that for different negative collector potentials, other discharge tube conditions remaining the same, the positive ion currents to the collector should be proportional to the sheath areas while the secondary elec-

[12] Schottky, Ann. d. Physik **62,** 143 (1920).
[13] Oliphant, Proc. Roy. Soc. **124A,** 228 (1929); **127A,** 373 (1930).
[14] Uyterhoeven and Harrington, Phys. Rev. **36,** 709 (1930).

tron emission, since chiefly due to metastable atoms, should remain practically constant, we found by the trial and error method, values of positive currents quite accurately proportional to the sheath areas (recalculated for these smaller currents) when we subtracted some certain constant value from our measured collector currents, these constant values being in general fairly reasonable ones for the secondary electron current when compared with Oliphant's,[13] and Uyterhoeven and Harrington's[14] results. In column 9 of Tables II, III and IV are tabulated the current values obtained in this way. The value followed by a negative sign and recorded between the first and second positive values is the assumed value of the secondary electron emission for the given discharge condition, since it was the necessary constant amount to be subtracted from the measured currents to give positive ion currents proportional to the corrected sheath areas. The last two positive ion current values in argon are slightly higher than they should be on this theory but this could be accounted for by the fact that under the existing conditions the secondary electrons would produce an appreciable amount of ionization within the sheath. To obtain results consistent with those for the higher accelerating voltages some of the measured currents in neon and helium for the lowest potentials used (about 21 volts) had to be increased by from 1 to 12 percent, amounts practically the same as those obtained by extrapolating the plots of the logarithm of the current against applied voltage, used in determining space potentials, and thus may be ascribed to the fraction of electrons having random energies greater than about 21 volts. The current values marked with a superscript c in column 3 are the ones so corrected.

The calculations made as for the results given in columns 7 and 8, Tables II, III and IV but using the positive ion currents given in column 9 instead of those given in column 3 led to the ratios of measured heating to expected heating (or accommodation coefficients) given in columns 10 and 11 for $\phi_+ = 0$ and $\phi_+ = V_i - \phi_-$ respectively.

Discussion of Results

Of the results given in columns 7, 8, 10 and 11 of Tables, II, III and IV the ones enclosed in parentheses are probably rather inaccurate, the ones with the superscript E being uncertain because of poor experimental conditions, the ones with superscript F are probably too high because the secondary electron current given by Found's assumption is unreasonably high in this case, and the ones with superscript H being probably too high because an assumption used in determining the fraction of energy not to be expected to reach the collector leads to a value for this fraction which is increasingly too high as the mean free paths become shorter, and the collision number increases. The assumption in question is the one given in parenthesis on page 1603 in connection with Fig. 3. Thus the nearer the point P is to the collector the greater will be the excess of molecules given direction outside of PT when struck by positive ions at P, but which later strike the collector as a result of collisions with other molecules, over those going outward across PT after being given directions inside PT when struck at P, since the distances which

the former must go before getting completely away from the collector are considerably greater than the distances the latter must go to reach it.

A study of the remaining values of the results shows that in helium the "accommodation coefficient" (hereafter referred to as A) increases as the positive ions are given higher velocities. This is in accord with the observations of Kingdon and Langmuir[15] that helium ions penetrate to a considerable depth into the metal which they are bombarding, an effect which would increase with increasing energy of the ions. In argon there appears to be no increase in A with increasing energy of the ions and in neon the effect is only very slight and we have neglected it in determining the mean values given for this gas in Table VII.

TABLE VII. *Summary of mean values of "accommodation coefficients."*

Column	Argon		Neon		Helium	
	Mean	Average variation	Mean	Average variation	21 to 51 V	111 to 141 V
7	0.770	0.023	0.674	0.019	0.40	0.56
8	.725	.029	.591	.038	.20	.47
10	.875	.056	.740	.022	.50	.70
11	.825	.047	.659	.033	.28	.56
Estimate of true value	0.75 ± 0.05		0.65 ± 0.05		0.35 ± 0.05	0.55 ± 0.05

In this table are given the means of the undoubtful values given in columns 7, 8, 10 and 11 of Tables II and III along with the average variations from the means. These average variations from the means are given not because we believe them to be a measure of the absolute accuracy of the results but because they give a concise method of showing the constancy of the results obtained under the four different assumed conditions on which the calculations of the four columns were based.

As judged by constancy, the results in argon would indicate that the actual secondary electron emission from the collector under our experimental conditions in this gas was probably considerably less than the approximately 25 percent given by Found's[3] assumption, and thus are in accord with the finding of only about 1 percent by our direct measurements of the emission from the auxiliary plate. Though the assumption of positive ion currents proportional to sheath areas gives in general reasonable values for the secondary electron currents the following considerations indicate that it is probably only an accident that the assumption does give such results. That the positive ion current is *not* controlled by the sheath area as given by the space charge equation but by a much larger volume, is certain. First, it is easily shown that the electrons, which penetrate within such sheaths surrounding our collector, could produce at most only a very small portion of the positive ions which

[15] Kingdon and Langmuir, Phys. Rev. **22**, 148 (1923).

are actually observed. Second, recent work of Langmuir,[16] and Tonks and Langmuir[2] has shown that, whereas most of the potential drop is within these sheaths, the positive ions which are collected are formed within a much larger volume. Hence there is no reason for believing that positive ion currents should be accurately proportional to such sheath areas, and hence the assumptions which underlie columns 10 and 11 of Tables II, III and IV appear to be unjustified. The values and discussion are included principally to illustrate how moderately large secondary electron currents would affect the results, if present.

Though the actual boundary of the region from which positive ions are drawn to the collector, is shown by the above considerations to be far outside of that given by the space charge equation, the latter value is not far from the boundary of the region into which any appreciable number of external electrons penetrate, and the greater part of the potential drop is between this boundary and the collector. Consequently we believe we are justified in using the space charge equation values for the sheath thicknesses in our calculations of the deflections and energy losses at collisions.

By carefully considering the various factors involved and the effect which changes in the assumed values of ϕ_+ and secondary electron emission have upon the results, we arrived at the estimates given for the true values of A for argon, neon and helium positive ions given at th : bottom of Table VII. These values are of the same order of magnitude as the values of A found by Knudsen[5] for cool gases striking a hot filament.

The "Umladung" effect described by Kallmann and Rosen,[17] Penning and Veenemans,[18] and others, i.e., the taking of an electron from a neutral molecule by a positive ion, the now neutralized ion retaining practically all of its kinetic energy and the new ion starting with negligible velocity, would increase the values of A slightly for the conditions giving the larger collision numbers but this effect would probably not be greater than the 0.05 possible error given in our estimates, particularly in argon for in this gas we have values for conditions under which collisions within the sheath are practically negligible.

That the energy given up by positive ions which have been attracted to a metal collector by a field should be less than the total kinetic energy of the ions is to bé expected from the explanation of the mechanism of cathode sputtering advanced by Kingdon and Langmuir,[15] and from the observations of Oliphant[13] and others on the reflection of positive ions and metastable atoms, and the probability of the formation of metastables in the neutralization process. If all of the observed deficiency of energy transfer were due to the formation of metastable atoms all of which left the collector with the velocity of the positive ions from which they were formed, this deficiency would give a measure of the production of metastables in the neutralization

[16] Langmuir, Phys. Rev. **33,** 954 (1929).
[17] Kallmann and Rosen, Zeits. f. Physik **61,** 61 (1930); **64,** 806 (1930).
[18] Penning and Veenemans, Zeits. f. Physik **62,** 746 (1930).

process. However, it is very improbable that the conditions are so simple as this.
velocity of the positive ions from which they are formed, this deficiency would give a measure of the production of metastables in the neutralization process. However, it is very improbable that the conditions are so simple as this.

In conclusion we wish to point out that although there is some uncertainty in the exact values of the accommodation coefficients for argon, neon and helium positive ions as found by us, our measurements seem to show conclusively that they are all considerably less than unity and consequently conclusions which have been reached on the tacit assumption of the unity value need revision to take account of the actual, smaller values.

Since the values of the accommodation coefficient found for neutral molecules[5] becomes more nearly unity as the molecular weight increases and since the values found by us for ions are of the same general order of magnitude as those found for the neutral molecules, it is suggested tentatively that the values for mercury and other heavy ions are nearly unity. Also the value of A is likely to depend somewhat upon the factors which affect the surface conditions of the metal such as the gas pressure, purity of the gas, roughness of the surface, and kind of metal.

Our thanks are due Mr. Donald C. Archibald for his help in the experimental work of this paper.

PHOTOMETRIC STUDY OF THE APPEARANCE OF SPECTRAL LINES IN A CONDENSED SPARK

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Abstract

The time interval between the time of appearance in a condensed spark discharge of the arc lines 4678A, 4722A, 4811A ($2^3P_{012}-2^3S_1$) of zinc, 4680A, 4800A, 5086A ($2^3P_{012}-2^3S_1$) of cadmium, the air lines 4347A, 4631A and 5001A was measured visually, using the Kerr cell method developed by Beams. A photographic method was developed whereby it was possible to determine from photometric measurements the variation of the intensity of an individual line with the time after the beginning of the spark. The time of first appearance, or zero intensity, is inferred from the extrapolation of the curves showing the intensity as a function of the time. The arc lines of zinc appear simultaneously. The arc lines of cadmium appear simultaneously but definitely earlier than the zinc arc lines. The air lines appear simultaneously but earlier than the arc lines. The spark lines appear simultaneously but earlier than the arc lines and later than the air lines of the respective elements. The results of the visual and photographic methods do not agree. Neither method gives information that in the case of zinc or cadmium, an electron remains in the 2^3S_1 state for a longer time before dropping to the 2^3P_0 state than before dropping to the 2^3P_1 or the 2^3P_2 state.

Introduction

In 1925 Beams and Brown,[1] making use of a modified form of the electro-optical shutter of Abraham and Lemoine,[2] measured the time intervals between the appearance of spectral lines in the spectra of condensed discharges. This early work indicated that in the elements examined, the spark lines appeared before the arc lines. Since the appearance of this first paper, several experimenters[3,4] have extended the work to other elements. In the elements that were examined in common by various investigators the numerical values for the time difference between the appearance of individual lines did not agree and in some cases the observed order was different. In the case of multiplets, Beams found different lines of the same multiplet appeared at different times, while Locher found that members of a given multiplet appeared simultaneously within the limits of error of the experiment in all cases examined except in the case of the arc triplet of zinc.

The actual existence of these time lags in the appearance of spectral lines has since been questioned by Gaviola.[5] He believes that the basic assumptions made by the experimenters, namely, that the Kerr cell discharges in-

[1] Beams and Brown, J.O.S.A. & R.S.I. **11,** 11 (1925).
[2] Abraham and Lemoine, Comptes Rendus **130,** 245 (1900).
[3] J. W. Beams, Phys. Rev. **28,** 475 (1926).
[4] Gordon Locher, J.O.S.A. & R.S.I. **17,** 91 (1928).
[5] Gaviola, Phys. Rev. **33,** 1023 (1929).

stantaneously a certain time after the beginning of the spark, that oscillations, if present, have no appreciable effect on the operation of the shutter, and that the capacity in parallel with the spark gap does not modify the time at which the Kerr cell discharges, are incorrect and measurements based on them unreliable.

The purpose of this investigation was to make a comparison of the results obtained by the use of a visual method similar to that employed by other experimenters[3,4] and the results obtained by use of a photographic method, in which the order of appearance of the spectral lines is inferred from the observations on the way in which the intensity of the individual spectral line

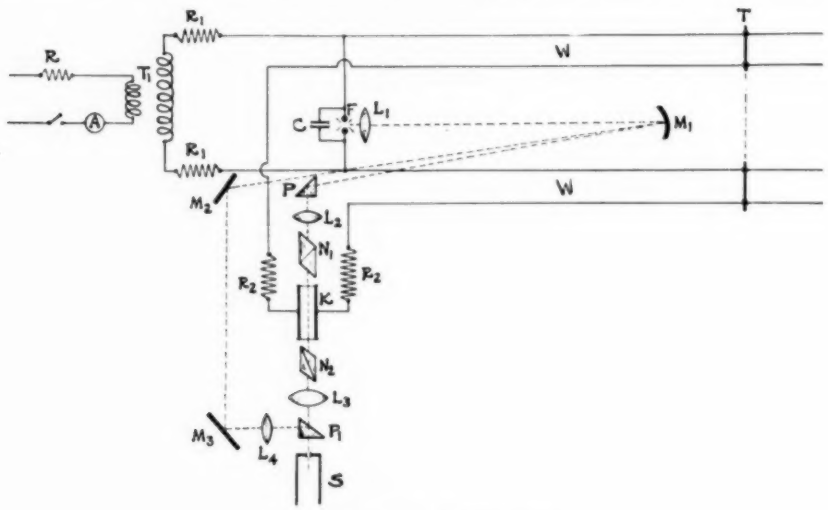

Fig. 1. Diagram of apparatus.

varies with time. By use of the latter method it is possible to eliminate the sensitivity of the eye which is a controlling factor in the visual method. In order that the results might have a possible interpretation as atomic phenomena, the spectral lines, 4678 $2^3P_0-2^3S_1$, 4800 $2^3P_1-2^3S_1$, 5086 $2^3P_2-2^3S_1$, of cadmium and 4680 $2^3P_0-2^3S_1$, 4722 $2^3P_1-2^3S_1$, 4811 $2^3P_2-2^3S_1$, of zinc were selected for the major part of this investigation. In the above triplets the transitions are from the same upper level to different lower levels, so the difference in the length of time that an electron remains in the 2^3S_1 state before the transition takes place to the 2^3P_0, the 2^3P_1 or the 2^3P_2 state could be measured. In addition to the above lines the spark doublet 5337 $3^2D_{3/2}-4^2F_{5/2}$, 5378 $3^2D_{5/2}-4^2F_{7/2}$ of cadmium, the spark doublet 4912 $3^2D_{3/2}-4^2F_{5/2}$, 4924 $3^2D_{5/2}-4^2F_{7/2}$ of zinc and the air lines which were excited when the discharge takes place between metallic electrodes in air at atmospheric pressure, were investigated.

Apparatus and Experimental Methods

Fig. 1 gives a diagrammatic representation of the apparatus used in the present experiment. It is essentially the same as that used by previous inves-

tigators. A fixed light path of 14.69 meters was used. A spark gap F with a capacity in parallel was connected across a source of high voltage T_1. The electro-optical shutter consisting of the two Nicol prisms N_1 and N_2 and the Kerr cell K, was placed between the spark gap and the spectrograph. The source of high voltage was a 25,000 volt 1 KW transformer. Electrodes of various shapes were tried in the spark gap, the shape finally selected being that of the frustrum of a cone, so that the discharge was actually taking place between two circular parallel faces. This type of electrode gave very steady spark conditions over quite long periods of time. The Kerr cell consisted of two parallel brass plates 12 cm long, 1 cm wide and separated at a distance of 3 mm, immersed in carbon disulphide which had been carefully purified. The shutter ordinarily was closed except when sufficient potential was applied to the Kerr cell, then the liquid became doubly refracting and light could pass it.

The circuit FC in Fig. 1 contains the condenser C, a certain amount of inductance in the lead wires, and the spark gap F, hence the discharge of the condenser C through the gap will be oscillatory. The circuit KF contains the Kerr cell, the trolley wires W and the spark gap F, this circuit being directly connected to the circuit FC, so oscillations are undoubtedly present in it. These oscillations if of sufficient amplitude, would reopen the shutter after having closed when the original voltage had fallen to so low a value as to make the shutter inoperative. The discharge of the Kerr cell will not be as sudden as was originally supposed, but its rate of discharge will be determined somewhat from the superposition of the oscillations in the two circuits. The oscillations can be critically damped by insertion of the resistance R_1, this reducing the rate of fall of voltage on the Kerr cell. Nevertheless it is possible to damp sufficiently these oscillations without delaying the closing time of the shutter appreciably, since it is well established that the relative difference in phase in the components of the ray vibrating parallel and perpendicular to the electric field is given by

$$\theta = 2\pi BlE^2$$

where B is the Kerr constant and θ the phase difference. Now the amount of light passing the prism N_2 at any given instant will be

$$I = A \sin^2 \theta/2 = A \sin^2 (\pi BlE^2).$$

Since the intensity of the light passing the shutter is proportional to the fourth power of the voltage, it is thus possible to damp sufficiently these oscillations and yet not delay the closing time of the shutter. The value of R_2 was found experimentally using a method employed by Lawrence,[6] that of observing the smallest distances of migration of the metallic vapor from the electrodes. The value of the damping resistance thus found was 2800 ohms (1400 ohms being placed in each lead from the spark gap to the Kerr cell). The effect of this damping resistance was quite evident, for when values of several hundred ohms less than 2800 ohms were used, oscillations were pres-

[6] Lawrence and Dunnington, Phys. Rev. **35**, 396 (1930).

ent, when values of several hundred ohms greater than 2800 ohms were used, a noticeable decrease in the rate of closing of the shutter was observed.

In Fig. 1 the light from the spark gap was rendered approximately parallel by the lens L_1 and was reflected from the concave mirror M_1, whose focal length was 7 meters, this converging beam was reflected by the right angle prism P through the lens L_2, the Nicol prism N_1 and focused between the plates of the Kerr cell. The lens L_3 focused the beam after passing through the Nicol prism N_2 on the slit of a constant deviation Gaertner spectrometer, so that the length of the spark was parallel to the slit. A number of diaphragms were placed along the light path and at each end of the Kerr cell so that only light which passed through the Kerr cell between the plates was focused on the slit.

An important modification in the optical path was the introduction of the auxiliary light path $PM_2M_3L_4P_1$, in order to adapt the apparatus to the photographic method. The part of the converging beam which passed the prism P was reflected by the plane mirrors M_2 and M_3 and the right angle prism P_1 and was focused on the slit of the spectrograph by means of the lens L_4. It was thus possible to have two spectra formed on the plate one directly above the other, the one formed by light which had passed through the Kerr cell and the other formed from the light which came directly from the spark gap. This modification was of utmost importance in the intensity measurements for it was thus possible to determine whether or not the spark conditions had changed appreciably during the time that was necessary to obtain a complete set of exposures.

Visual method. In the visual method in which a fixed light path was used, the time of closing the electro-optical shutter was regulated by changing the effective lengths of the four parallel wires which connect the spark gap with the Kerr cell, by sliding the trolley T along them by means of a string passing over a rather complicated pulley system and operated from the observer's position. When the trolley T is adjusted so that the effective length of wire path is as long as possible the intensity of the line under investigation is at a maximum for this particular time of closing of the shutter. If the position of the trolley is now adjusted so that the length of the wire path is decreased, finally a position is reached where the spectral line is no longer visible; this position of the trolley is noted. In a similar manner when the direction of motion of the trolley is reversed, a point of first appearance of the spectral line is located, which will differ slightly from the first position. The mean of the two positions is taken as the position of first appearance of the line, where the appearance of the line as used here means the position at which the line has become visible through the observing apparatus. The fall of potential produced by the passage of the spark is propagated along the wire to the Kerr cell at approximately the velocity of light,[7] so that the difference between the times of appearance of two lines is approximately the difference between the lengths of wire as determined above, divided by the velocity of light.

[7] Fred Allison, Phys. Rev. **30**, 66 (1927).

Photographic method. In the photographic method the observing telescope was replaced by a camera attachment converting the spectrometer into a spectrograph. The optical path was modified as previously described. The exposures on the plate were obtained by setting the trolley at a definite position and taking an exposure, then moving the trolley a known distance and taking a second exposure, and so on until five or more exposures had been obtained on each plate. Since the lengths of trolley wire between the spark gap and the Kerr cell correspond to lengths of time after the break down of the

TABLE I. *Zinc, cadmium and nitrogen.*

The nitrogen lines were obtained by a discharge between zinc electrodes in air. The zinc and cadmium lines were obtained from discharges between electrodes made from the chemically pure metals.

Element	Wave-length	Classification	Interval $\times 10^8$ sec.	Limit of error $\times 10^8$ sec.
Zn	4912 & 4924	$3^2D_{1\frac{1}{2}}-4^2F_{2\frac{1}{2}}$ & $3^2D_{2\frac{1}{2}}-4^2F_{3\frac{1}{2}}$		
			0.5	.06
Zn	4680	$2^3P_0-2^3S_1$		
			1.14	.04
Zn	4722	$2^3P_1-2^3S_1$		
			0.75	.04
Zn	4811	$2^3P_2-2^3S_1$		
Cd	5337 & 5378	$3^2D_{1\frac{1}{2}}-4^2F_{2\frac{1}{2}}$ & $3^2D_{2\frac{1}{2}}-4^2F_{3\frac{1}{2}}$		
			0.43	.05
Cd	5086	$2^3P_2-2^3S_1$		
			0.97	.12
Cd	4800	$2^3P_1-2^3S_1$		
			0.37	.08
Cd	4678	$2^3P_0-2^3S_1$		
N_2	5001	$1^3D_1'-1^3F_3'$		
	5005	$1^3D_3'-1^3F_4'$		
	5007	$1^3S_1'-1^3P_2''$		
	5011	$1^3P_1'-1^3S_1'$		
			1.20	.15
N_2	4631 & 4643	$1^3P_2'-2^3P_2$ & $1^3P_2'-2^3P_1$		
			1.92	.08
N_2	5676 & 5680	$1^3P_0'-1^3D_1'$ & $1^3P_2'-1^3D_3'$		

gap, the position of the trolley can be plotted against the intensity of the spectral line and a curve obtained which will show how the intensity of an individual line varies with time. In the present experiment it was possible to obtain spectrograms of the light from the spark beginning at 3.9×10^{-11} seconds after the beginning of the spark to 1.4×10^{-7} seconds after the beginning of the spark, the range being limited by the lengths of wire in the set-up.

Each plate was carefully calibrated by the use of neutral screens.[8] The calibration curve was obtained by plotting the logarithm of the intensity of the light transmitted by these screens against the reciprocal of the photographic density upon the plate. The reciprocal of the density (the logarithm of the transmission of the plate) was determined from the microphotometer record which was secured from the spectrogram. A Moll microphotometer which records automatically was used. From the measured transmission of the metallic arc and spark lines and the air lines to be investigated, the intensity of the individual lines could be read directly from the calibration curves in arbitrary units.

Results

Results by the visual method. Table I contains the data obtained on the spectral lines which were examined in this experiment. In the case of zinc the order of appearance of the lines obtained in this experiment was the same as that reported by Beams.[3] The magnitude obtained for the interval between the first appearance of the spark lines 4912A, 4924A and the arc line 4680A is thirty times smaller than the value obtained by Beams. In cadmium the results for these corresponding lines differ by about the same amount, that is for the interval between the appearance of the spark lines 5337A, 5378A and the first arc line. However the order is not the same, for in this experiment 5086A was observed before 4800A, while Beams observed them in the reverse order. The time intervals between the appearance of the respective arc lines as measured by Beams show somewhat the same magnitude as those determined in this experiment, but the results are still far from agreement. Locher obtained no differences in the times of appearance of the cadmium arc lines.

Results by the photographic method. The data obtained for the arc triplet of zinc 4680A, 4722A, 4811A are plotted in Fig. 2. The intensity which is plotted as the ordinate is expressed in arbitrary units. The lengths of trolley wire, plotted as abscissa, are measured from an arbitrary reference point which corresponds to a time 5×10^{-11} sec., after the beginning of the spark. When the intensity curves for these lines are extrapolated backward they all intersect at a point on the time axis corresponding to a time 1.2×10^{-8} sec., after the beginning of the spark, indicating that the members of this arc triplet appear at the same time. Fig. 3 shows the data on the unresolved air lines 5001A, 5005A, 5007A and 5011A, 4631A, 4347A which were excited when the discharge occurred between zinc electrodes in air at atmospheric pressure. Here as in the case of the metallic arc lines of zinc, when the intensity curve for each of these lines is extrapolated backward to zero intensity, these curves meet at approximately the same point, corresponding to a time 5×10^{-11} sec. after the beginning of the spark. This would indicate that these lines appeared simultaneously, but at a time 1.19×10^{-8} sec. earlier than the metallic arc lines of zinc.

[8] G. R. Harrison, J.O.S.A. & R.S.I. **18,** 492 (1929).

Fig. 4 shows the curves plotted from the data obtained for the arc triplet of cadmium 4678A, 4800A, 5086A. The intensity curves meet at approximately the same point corresponding to a time 0.5×10^{-8} sec., after the beginning of the spark when extrapolated backward to zero intensity, indicating again that the members of this arc triplet all appear at the same time. The time of appearance of the cadmium triplet is 0.7×10^{-8} sec., earlier than the zinc triplet. Fig. 5 shows the data on the air lines 5001A, 5005A, 5007A, 5011A, 4631A, 4347A, which are excited when the discharge takes place between cadmium electrodes in air. When the intensity curve for each of these air lines is extrapolated backward to zero intensity these curves intersect at a point corresponding to the time 5×10^{-11} sec., after the beginning of the spark, which is the same as that obtained for these same air lines which were

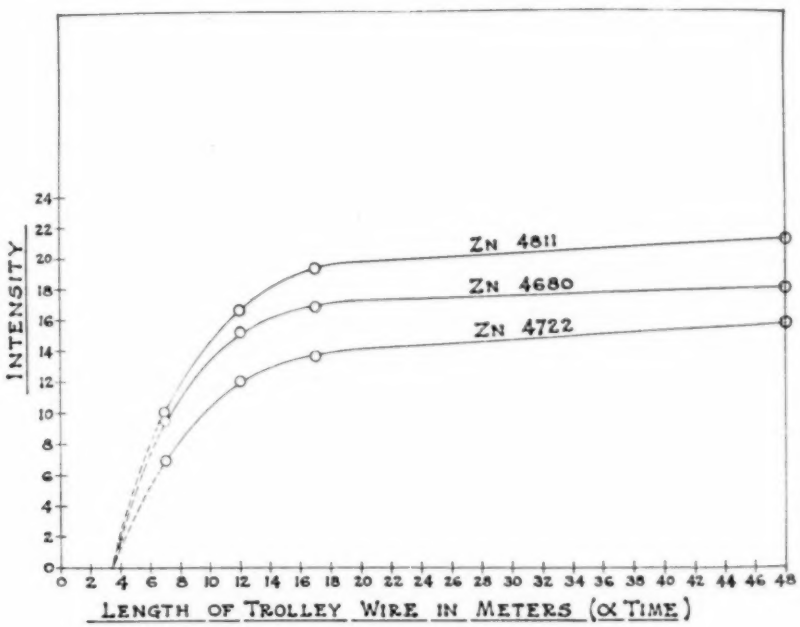

Fig. 2. Intensity of zinc arc triplet ($2^3P_{012}-2^3S_1$).

excited in the zinc spark. This indicates that these air lines just as in the case of zinc all appear at the same time.

In the upper part of Fig. 6 are plotted the data obtained for the unresolved zinc spark doublet 4912A and 4924A, and in the lower part are plotted the data obtained for the cadmium spark doublet 5337A and 5378A. The unresolved zinc doublet extrapolates backward to a point corresponding to 0.5×10^{-8} sec., after the beginning of the spark. The intensity curves for each of the lines of the cadmium doublet, when extrapolated to zero intensity, meet at a point corresponding to a time 0.32×10^{-8} sec., after the beginning of the spark, indicating that each of the members of this spark doublet appeared at the same time. The time of zero intensity or the time of first appearance of

the spark lines is earlier than the arc lines of the same element, but is later than the air lines as shown in Figs. 2, 3, 4, and 5.

Discussion of Results

The photographic method in the case of the arc triplet of zinc 4680A, 4722A and 4811A, shows that all of these lines appear at the same time. The visual method when applied to this same triplet gives differences between the times of appearance of these same lines. Likewise in the case of the arc triplet of cadmium 4678A, 4800A and 5086A the photographic method gives the same time of appearance for each of these lines, but the visual method gives different times for each line, although the results of different observers using the visual method are not in agreement.

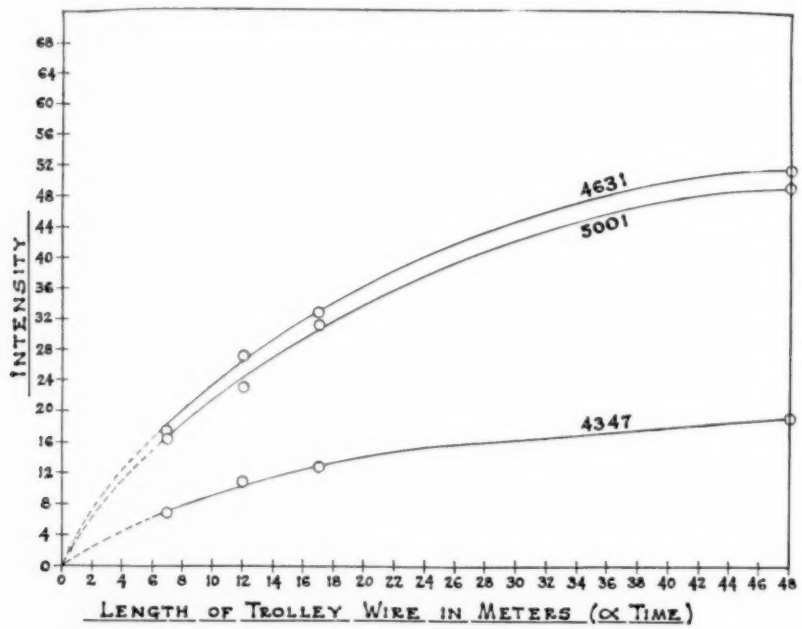

Fig. 3. Intensity of the air lines 5001A, 4631A, and 4347A with zinc spark gap.

The photographic method shows that the air lines 5001A, 5005A, 5007A, and 5011A, 4631A, 4347A whether excited in a zinc or cadmium spark, all appear at the same time, but at a time definitely earlier than the metallic arc lines of the respective element. The visual method on the other hand gives different times of appearance for the individual air lines and it also indicates that the air lines appear before the arc lines in the case of zinc and cadmium. Since in this case the observations were made on groups of lines rather than individual lines, the results are not as convincing as in the case where the observations are made on separate lines.

The photographic method shows that the members of the spark doublet of cadmium 5337A and 5378A appear at the same time and definitely earlier than the metallic arc lines of cadmium, but later than the air lines in the cad-

mium spark. The visual method gave no information on the separate spark lines as it was impossible to resolve them, so the observations were made probably on both lines, the times of appearance being earlier, however, than the arc lines. The result, indicating that the spark lines appeared before the arc lines, is the same for each method. The zinc doublet 4912A and 4924A was unresolved in both the photographic and visual methods so that the data obtained in each case are not satisfactory. However each method shows that this unresolved zinc doublet appears before the zinc arc triplet, hence again the two methods lead to the same result.

There is an evident disagreement between the results obtained by the visual method and those obtained by the photographic method. This diver-

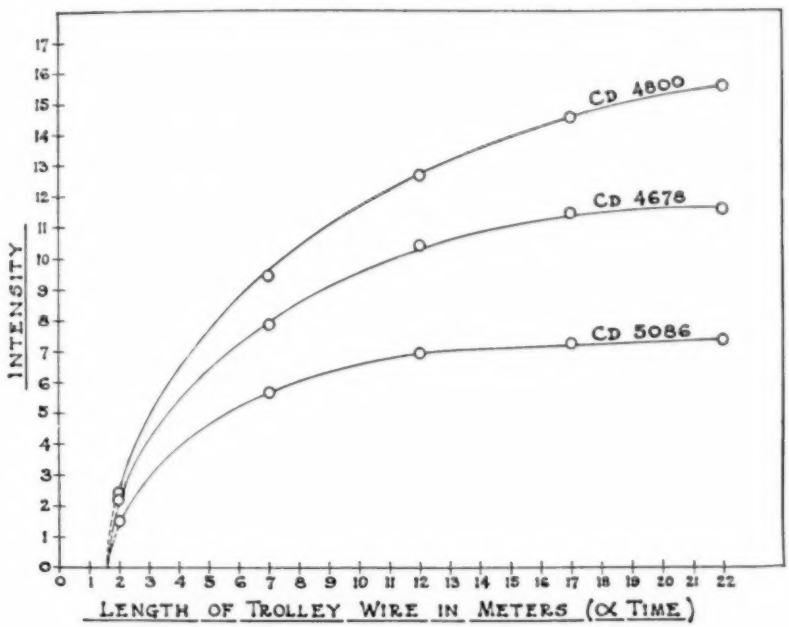

Fig. 4. Intensity of the cadmium arc triplet ($2^3P_{012}-2^3S_1$).

gence of results is to be expected from the fact that the human eye is not equally sensitive to light of different colors, whereas the photographic plate when properly calibrated should give results on relative intensities which are independent of the sensitivity of the plate for light of different wave-lengths. Hence the zero of intensity inferred from the measurements on the photographic plate would be different from the threshold of visibility detected by the human eye. In reality what one does in the visual method is to observe the line at some intensity considerably above the zero intensity. Examination of the curves, showing the intensity as a function of the time after beginning of the spark, shows that the times when the different lines have the same intensity is variable. The critical intensity which the eye could first detect would be influenced by the sensitivity of the eye for the particular wave-length. The lines which were examined were located in a region of the spectrum

where the sensitivity of the human eye changes quite rapidly with the wavelength. It would be impossible to extrapolate the intensity curves shown in Figs. 2, 3, 4, 5 and 6 in a reasonable manner and obtain values for the relative differences in the times of appearance that were obtained visually. The calibration of the photographic plate made the results obtained by the photographic method independent of the sensitivity of the plate for different colors. The fact that the air lines appeared before the spark and arc lines of the respective elements is probably a result of the natural sequence of events in breakdown of the spark gap. One might suppose as Gaviola[5] suggested, that the discharge was initiated by ionizing the air between the electrodes. This was followed by evaporation of the metal from the electrodes which was then ionized and excited by collisons. This observed difference between the

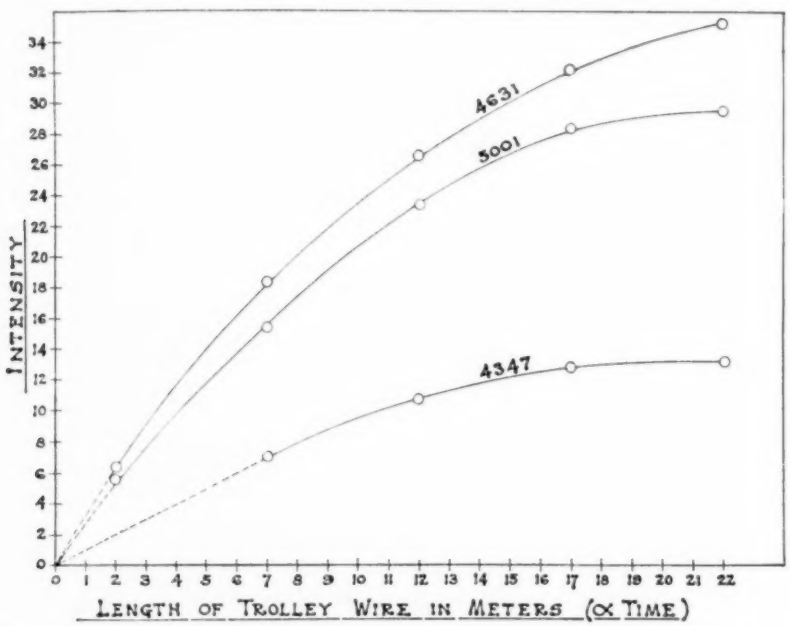

Fig. 5. Intensity of air lines 5001A, 4631A, and 4347A with cadmium spark gap.

times of first appearance of the air lines in the zinc and cadmium spark and the metallic arc lines of the same elements may be explained as a characteristic of the spark discharge. Hence if the results of the photographic method are accepted, the data obtained in this type of experiment give no evidence that an electron in the 2^3S_1 state of zinc or cadmium remains there a longer time before the transition takes place to the 2^3P_0 state, than to the 2^3P_1 or the 2^3P_2 state.

Conclusions

1. The results obtained by the visual and photographic methods are not in agreement.

2. The results obtained by the photographic method indicate that the members of the arc triplet of zinc appear simultaneously. They also indicate

that the members of this same triplet of cadmium appear simultaneously but not at the same time as the members of the arc triplet of zinc. These results therefore seem to verify Gaviola's contention that the apparent time difference between the appearance of spectral lines in such condensed discharges is not an atomic phenomenon.

3. The differences in times of appearance between the air lines which are excited in the spark gap, the spark lines of the element and the arc lines of

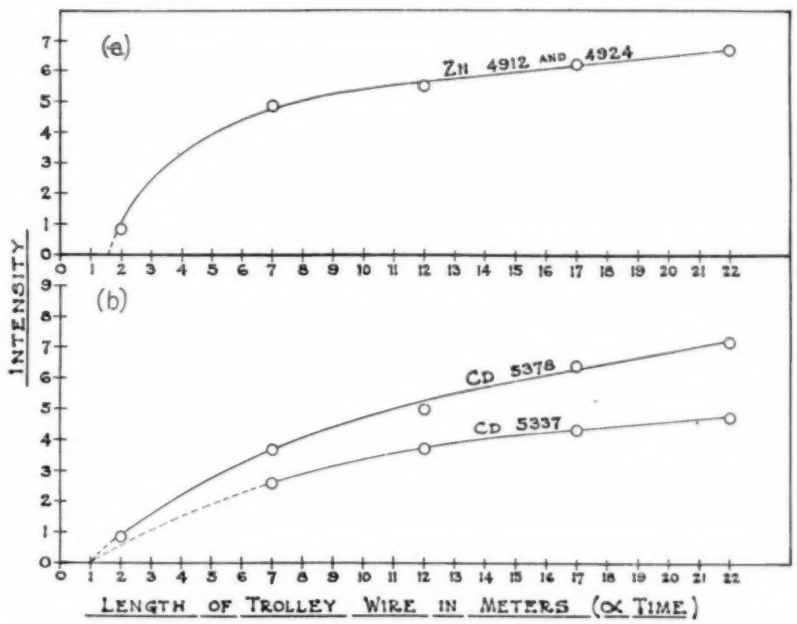

Fig. 6. (a) Intensity of unresolved zinc doublet ($3^2D_{3/2}-4^2F_{5/2}$) and ($3^2D_{5/2}-4^2F_{7/2}$). (b) Intensity of cadmium doublet ($3^2D_{3/2}-4^2F_{5/2}$) and ($3^2D_{5/2}-4^2F_{7/2}$).

the same element, can probably be attributed to the way in which the discharge is formed in the spark gap, i.e. the manner in which the molecules of air or vapor of the element begin to be ionized.

The writer wishes at this time to express his appreciation of the constant help and encouragement he has received from Professor Alpheus W. Smith under whose direction this work was carried out and of the valuable suggestions and criticisms received from Dr. M. L. Pool during the course of this work.

THE EFFECT OF PIEZOELECTRIC OSCILLATION ON THE INTENSITY OF X-RAY REFLECTIONS FROM QUARTZ

By Gerald W. Fox and Percy H. Carr
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(Received May 1, 1931)

Abstract

In an attempt to determine the amplitude of vibration of the ions in a quartz lattice brought about by piezoelectric oscillations, a series of Laue photographs have been made of both Curie and thirty-degree-cut plates, using the white radiation from a Coolidge universal tube. This tube had a tungsten anode and carried a current of four milliamperes at 95 kilovolts. Eastman duplitized x-ray film was used with no sensitizing screens. On examination, the patterns produced by each plate, oscillating and non-oscillating, appear identical except in one respect; the pattern of the oscillating plate is several times as intense as that of the non-oscillating. A four-hour exposure of a non-oscillating plate to radiation of the above mentioned type, produces but the rudiments of a pattern, whereas, the same plate oscillating produces a very beautiful intense pattern for the same time of exposure. The effect does not depend on the mode of vibration but does depend on the amplitude. Further work is in progress which it is hoped will establish the cause of this peculiar intensity difference.

Introduction

PIEZOELECTRIC quartz plates used as frequency controllers for vacuum tube oscillators have a visible vibration[1] when in mechanical resonance with the electrical circuit. Such mechanical oscillations must be accompanied by considerable internal movement of the ions of the crystal lattice. It was proposed to investigate this internal motion by shooting a beam of x-rays through a quartz plate both when oscillating and when not oscillating and by observing whether there was any difference in the appearance of the Laue diffraction patterns.

If there was considerable motion of the crystal planes, it might be expected that the spots on the Laue pattern would be altered. Upon first consideration, one might think that this alteration would occur either as a linear smearing of the spots or as a diminution in the intensity of the pattern. The first hypothesis seemed reasonable because of the experiments of Professor Joffé[2] in which a linear smearing of the spots was produced by a mechanical distortion of the crystal. The second hypothesis appeared reasonable from temperature consideration. The usual result of raising the temperature of a crystal is that the reflection slowly decreases almost linearly with increase in temperature. Backhurst[3] gives some data on graphite and ruby, finding a fifteen percent decrease in reflecting power for a rise in temperature of 500° Centigrade.

[1] H. Osterberg, Nat. Acad. Proc. **15,** 892 (1929).
[2] Joffé, The Physics of Crystals, p. 38.
[3] Backhurst, Proc. Roy. Soc. London **102,** 340 (1922).

Gibbs[4] called attention to the unusual increase in reflecting power of certain planes in crystal quartz which took place at the transition temperature (575°C) when the so-called α form changed over to the β form. Since this large increase was attributed to a relative movement of the ionic planes of only 0.025 Angstrom unit, it seemed possible that oscillations in quartz might produce a change in the relative intensity of the Laue spots.

Apparatus and Methods

Eastman duplitized x-ray films were used throughout. Sensitizing screens were tried at first but were soon discarded for fear they might influence results. The film was placed in a box made of 1/8″ lead sheet closed except for a small 1/2″ hole in the top. Directly above this hole was mounted in intimate contact, the lower contact plate for the crystal, made of brass and polished flat. In its center was a 1/4″ hole. The upper contact plate of the crystal was also made of polished brass. In its center was drilled a 1/8″ hole. Radiation from a Coolidge universal tube was delimited by a number 60 drill hole in each of two lead screens mounted approximately five inches apart. Attached to the lower screen and in line with the hole was a two-inch narrow tube of

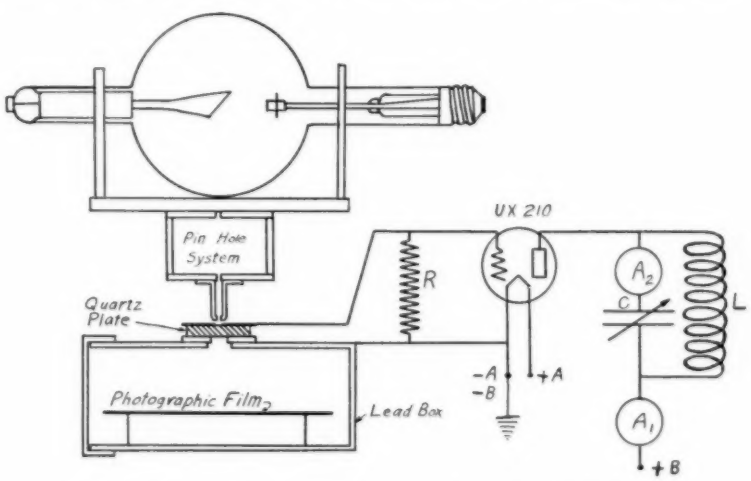


Fig. 1. Schematic diagram of x-ray tube and crystal circuit.

brass also having a number 50 drill hole in its end. This was merely to facilitate pointing the x-ray beam at the hole in the upper electrode.

The driving circuit is shown in Fig. 1, together with a schematic drawing of the whole layout. The vacuum tube was of the UX210 type employing a filament voltage of 7.5 volts. Plate voltages from 50 to a maximum of 350 volts were used at various times. Resonant conditions in the circuit were determined by observations of the D.C. plate milliameter A_1 or the radio frequency ammeter A_2. In this type of circuit using a resistance bias, oscillations are indicated by a large drop in the D.C. plate current and a corresponding increase in the reading of the high frequency ammeter.

[4] Gibbs, Proc. Roy. Soc. London **A107,** 561 (1925).

Results

A preliminary run with the non-oscillating crystal showed that at 95 kilovolts peak and 4 milliamperes x-ray tube current at least a four-hour exposure would be necessary to get even a visible pattern. With the same exposure, however, this same plate, oscillating, gave a very beautifully developed Laue pattern. This was curious, and since the exposure on the oscillating crystal had been made in two parts with a lapse of several hours between, and since the film had been developed at a different time and with a different solution than that of its non-oscillating mate, it was assumed that some difference in technique had produced the decided change in intensity. To test this point three different diffraction patterns were made of the same quartz plate; the first, with the plate not oscillating; the second with the plate oscillating; and

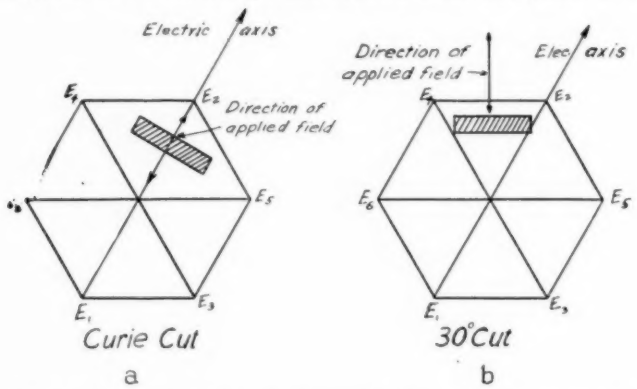


Fig. 2. (a) Curie-cut. In use the applied electric field is parallel to an electric axis of the crystal. The optic axis is normal to the plane of the figure. (b) 30-degree-cut. In use the applied electric field makes an angle of 30° with an electric axis of the crystal.

the third with it not oscillating again. In each instance, a four-hour continuous exposure was made at 95 kilovolts and 4 milliamperes. Over a four-hour period slight voltage-current fluctuations were bound to occur but an average current of four milliamperes over the necessary twelve-hour period is probably very close to the truth. All three exposures were then simultaneously developed in a single large tray and were fixed at the same time. Examination of all three films showed beyond doubt that the pattern made by the oscillat-

Table I

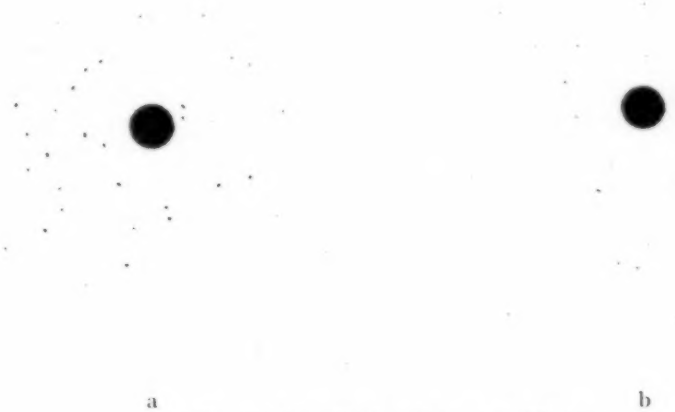
Curie-cut Frequencies (kilocycles)	30-degree-cut Frequencies (kilocycles)
3590	3850
1900	1875
320	325

ing plate was decidedly more intense than either pattern made by the non-oscillating plate. This discovery made it necessary to go into the phenomenon in more detail.

Six plates were cut from a specimen of optical quality crystal quartz, three of each type of cut as shown in Fig. 2. These plates were then ground down to the following approximate frequencies, as shown in Table I.

The Curie-cut plates have an average wave-length of about 105 meters per millimeter thickness and the 30-degree-cut, about 145 meters per millimeter thickness.

Two four-hour exposures were then made for each plate. Simultaneous development and fixing were carried out. In each case, the same result was obtained, viz.; *an exposure which gave but the rudiments of a pattern with the plate not oscillating, gave an intense pattern when the plate was vibrating.* Visual examination shows the patterns to be identical with the same spots occurring but the intensity is decidedly different. Fig. 3 shows a reproduction of the patterns produced by a 30-degree-cut plate, oscillating and not oscillating. This plate had an approximate frequency of vibration of 1875 kilocycles. It



a b

Fig. 3. (a) oscillating; (b) not oscillating.

was not possible to note any smearing of the spots as was suggested might happen though the method is too crude to detect small changes.

To test the possibility that the effect was due to some sort of an electric strain set up by the applied electric field, a test was run on the same plate whose pattern is shown in Fig. 3. Again two runs were made, the first with no applied field and the second with the line voltage of 120 volts, 60 cycles, applied to the crystal. Both exposures were identical. The two exposures proved to be no different showing that the effect is definitely a resonance phenomenon.

To test this conclusion further, the same piezo-plate was used in a series of three four-hour exposures. The x-ray energy was kept constant and the amplitude of vibration was changed by increasing the plate voltage on the vacuum tube. The voltages used were 50, 150, and 300 volts, respectively. The three exposures show definitely that the intensity of the spots on the patterns depends on the amplitude of vibration of the quartz plate. The 150 volt exposure is decidedly stronger than the 50 volt one and the 300 volt exposure is much stronger than either.

CRYSTAL STRUCTURE OF LITHIUM IODATE

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(Received April 22, 1931)

Abstract

The structure of lithium iodate was determined by using the oscillation and powder methods. Lithium iodate is hexagonal with 2 molecules per unit cell of $a=5.469\pm0.003$A, $c=5.155$A ±0.005A. The space group assigned is D_6^6 and the atom positions are: 2Li in (001/4) (003/4), 2I in (1/3 2/3 1/4) (2/3 1/3 3/4) and 6 O in ($uu0$) ($0\bar{u}0$) ($\bar{u}00$) ($\bar{u}\bar{u}\frac{1}{2}$) ($0u\frac{1}{2}$) ($u0\frac{1}{2}$) with $u=1/3$. The structure is based on hexagonal closest packing, with the lithium and iodine atoms both lying within oxygen octahedra. The atomic distances are Li$-$O and I$-$O$=2.23$A with lithium octahedra sharing faces with each other, one lithium and one iodine octahedra sharing only edges and two iodine octahedra only corners.

LITHIUM iodate is the only member of the alkali iodates, whose structure has not yet been determined.[1] In searching the literature no information was found regarding its crystallographic properties. A microscopic examination of the fine crystalline material of chemically pure $LiIO_3$ as furnished by Kahlbaum, showed that the crystals were short hexagonal prisms. Though $LiIO_3$ does not crystallize in very large crystals, two crystal splinters were found sufficiently large to be used for the oscillation method. Both crystals were hexagonal prisms and photographs were taken using the principal directions as axes of rotation. In view of the fineness of the material a large number of powder photographs were taken using Mo$K\alpha$, Cu$K\alpha$, and Fe$K\alpha$, radiation.

The photographs were worked out in the usual manner and lead to the following dimensions of the hexagonal cell.

$$a=5.469\text{A}\pm0.003\text{A} \qquad c=5.155\text{A}\pm0.005\text{A} \qquad c/a=0.9427$$

A rough density determination of $LiIO_3$ gave 1.9 molecules equivalent to 2 molecules per unit cell. The calculated density is 4.48. The greater part of the observations is compiled in Tables I and II. From the tables it is clearly seen that a rhombohedral cell is impossible because of the observed reflections. (The number of molecules in the hexagonal cell also exclude a rhombohedral lattice.) Since the oscillation photographs did not show any deviation from full hexagonal symmetry, consideration of the space group was limited to the following classes: D_{6h}^n, D_6^n C_{6v}^n and D_{3h}^n. Of these D_6^2 and D_6^5 were ruled out because they have no 2-fold (or 1-fold) positions.

Tables I and II show that whenever $2h+k$ is divisible by 3, exceptionally strong reflections are observed if l is even; whereas the intensity is weak or

[1] V. M. Goldschmidt, Vid. Akad. Skr. Oslo **2,** 79 (1926) KIO_3, $RbIO_3$; W. H. Zachariasen, ibid. **4,** 100, 106 (1928) $NaIO_3$, $CsIO_3$.

nil if l is odd. This observation can only be accounted for by putting the two iodine atoms in positions corresponding to a hexagonal closest packing of these atoms. The only available space groups compatible with such an arrangement are D_{3h}^1, D_{3h}^4, C_{6V}^4, D_6^6, and D_{6h}^4. The space groups D_{6h}^4, C_{6V}^4,

TABLE I. *Oscillation photographs.*

hk. l	sin θ	$\|F\|$	Int.	*hk. l*	sin θ	$\|F\|$	Int.
00.1	0.0687	nil	nil	22.0	0.2590	60.8	m
10.0	.0748	43.6	m	30.2	.2629	53.0	m
10.1	.1015	78.7	vs	22.1	.2679	13.5	nil
11.0	.1295	72.1	vs	31.0	.2695	30.4	vw
00.2	.1373	55.4	s	00.4	.2746	73.8	m
11.1	.1466	25.5	w	31.1	.2781	53.7	m−
20.0	.1496	37.4	m	21.3	.2856	54.6	m
10.2	.1564	36.9	m	22.2	.2932	68.0	m
20.1	.1645	65.4	s	31.2	.3024	28.0	vw
11.2	.1877	86.6	s	11.4	.3036	56.0	m
21.0	.1977	33.8	vw	32.0	.3258	27.0	vw
20.2	.2030	33.8	w	32.1	.3330	49.5	w
00.3	.2061	nil	nil	41.0	.3343	53.4	w
21.1	.2093	64.2	m	31.3	.3392	49.2	w−
10.3	.2192	61.5	s	41.1	.3413	9.4	nil
30.0	.2244	90.8	s	32.2	.3536	26.4	vvw
30.1	.2345	nil	nil	41.2	.3614	61.1	w
21.2	.2408	31.2	w	32.3	.3854	46.0	w
11.3	.2433	14.6	nil	41.3	.3926	7.3	nil
20.3	.2545	57.1	m−				

TABLE II. *Powder photographs.*

hk. l	sin θ	$\|F\|^2xf$	Int. Obs. Mo	Int. Obs. Cu	*hk. l*	sin θ	$\|F\|^2xf$	Int. Obs. Mo	Int. Obs. Cu
00.1	0.0687	nil	nil	nil	21.2	0.2408	3.9	w+	w
10.0	.0748	1.9	w+	w	11.3	.2433	.4		
10.1	.1015	12.4	vs	s	20.3	.2545	6.5		m
11.0	.1295	5.2	ms	m	22.0	.2590	3.7		w+
00.2	.1373	1.0	vw	vw	30.2	.2629	5.6		m
11.1	.1466	1.3	w	vw	22.1	.2679	.4		vw
20.0	.1496	1.4			31.0	.2695	1.9		
10.2	.1564	2.7	w	w	00.4	.2746	1.8		nil
20.1	.1645	8.6	ms	m	31.1	.2781	11.5		s
11.2	.1877	15.0	s	s	10.4	.2847	1.7		s
21.0	.1977	2.3	vw	w	21.3	.2856	12.0		
20.2	.2030	2.3	vw	w	22.2	.2932	9.2		m
00.3	.2061	nil			40.0	.2992	.8		
21.1	.2093	16.5	s	s	31.2	.3024	3.1		ms
10.3	.2192	7.6	m−	m−	11.4	.3036	6.3		
30.0	.2244	8.2	m	m−	30.3	.3045	nil		
30.1	.2345	nil	nil	nil	40.1	.3069	5.4		w

TABLE III. *F Curves (MoKα).*

sin θ	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
Li	2.0	1.9	1.8	1.6	1.3	1.1	.85	.7
I	50	45.5	41	37	33.5	31	28	26
O	8.0	7.5	4.9	3.0	2.7	2.1	1.6	1.3

The *F*-curve for iodine was calculated by Thomas' method, the one for oxygen is the experimental one found by J. West in KH_2PO_4.

and D_{3h}^4 are ruled out because they require that the odd order reflections from all planes $h\ k.l$ where $2h+k=3n$ and l odd shall be missing, and while many of these reflections are not found, there is evidence in the photographs that some of them are definitely present. This limits the space group selection to D_{3h}^1 and D_6^6.

In D_{3h}^1 in order to have hexagonal closest packing the necessity for unequivalent iodine atoms arises. The possibility that all oxygen atoms lie in the same plane is unreasonable as that would give too small oxygen to oxygen distances. Likewise this rules out the possibility that they all lie on 3-fold or 6-fold axis of symmetry. The only possible arrangements of the 6 oxygens are therefore: $3j+3k$ or $6n$ with $v=1/4$. None of these possibilities leads to reasonable structures.

In case the 6 oxygens are put in $3j+3k$ and the required oxygen to oxygen distance is greater than 2.50A, the iodine to oxygen distance is smaller than 1.72A. It seems improbable that the oxygen to oxygen distance is smaller than 2.50A, and that the iodine to oxygen distance is as small as 1.72A. This arrangement must therefore be ruled out and for similar improbabilities placing the 6 oxygens in positions $6n$ can not be considered.

As an additional support for ruling out the considerations of the previous paragraph are the intensity considerations. With the oxygen in $3j+3k$ it is impossible to explain the weak 00.2 reflection. Similarly if the oxygens lie in $6n$ the parameter v must be 1/4 in order to explain the absent odd orders from the basal plane, which would necessitate the absence of reflections 11.1, which as the tables show are definitely present.

The only remaining space group is D_6^6.

The 2 iodine atoms are put in positions (1/3, 2/3, 1/4) (2/3, 1/3, 3/4) in accordance with the required hexagonal closest packing. Since all the atoms can not lie on the 3-fold axes of symmetry, the only positions for the oxygens are $(uu0)$ $(0\bar{u}0)$ $(\bar{u}00)$ $(\bar{u}\bar{u}\frac{1}{2})$ $(0u\frac{1}{2})$ $(u0\frac{1}{2})$ or $(u\bar{u}\ 1/4)$ $(2\bar{u}\bar{u}\ 1/4)$ $(u2u\ 1/4)$ $(\bar{u}u\ 3/4)$ $(2uu\ 3/4)$ $(\bar{u}2\bar{u}\ 3/4)$. The latter arrangement does not account for the relative weak 00.2 reflection and therefore the first set is the correct one.

An accurate determination of the oxygen parameter cannot be made due to the small scattering power of these atoms in comparison with that of iodine. The powder photographs show that 30.0 and 30.2 occur with nearly the same intensity although the latter form has twice as many faces as the former. In order to explain this ratio the oxygen atoms must give a large positive contribution to the structure factor for both reflections. This requirement necessitates $u=1/3$. The value 1/3 is very probable as that gives us hexagonal close packing of the oxygens. A close packed arrangement of the oxygens (using oxygen to oxygen distance = 2.7A) would give us a cell of dimensions $a=$ 4.68A, $c=4.42$A with an axial ratio of 0.944. The fact that the experimental cell is larger than the theoretical one must be attributed to an expansion of the close packing due to the circumstance that both iodine and lithium are too large to fit in the interstices.

The lithium atoms are so light that their positions cannot be determined from the intensities of reflections. There are three sets of available positions

for lithium: (2a) (000) (00½); (2b) (00 1/4) (00 3/4) and (2d) (1/3, 2/3, 3/4) (2/3, 1/3, 1/4). The set (2a) will put lithium inside of an oxygen triangle with lithium to oxygen distance = 1.83A. Using (2b) or (2d) lithium will be within an octahedron of oxygens; the lithium to oxygen distance being 2.23A. The triangular arrangement of oxygens around lithium has never been found in other structures. Lithium either goes inside a tetrahedron of oxygens (Li_2O, $KLiSO_4$, Li_2MoO_4) or within an octahedran ($LiNO_3$). Of the latter two arrangements (2b) is the most plausible one, because this results in a lithium to iodine distance of 3.16A whereas (2d) would give 2.58A.

The complete structure thus determined is 2 Li in (00 1/4) (00 3/4), 2I in (1/3 2/3 1/4) (2/3 1/3 3/4) and 6 O in ($uu0$) ($0\bar{u}0$) ($\bar{u}00$) ($\bar{u}\bar{u}\frac{1}{2}$) ($0u\frac{1}{2}$) ($u0\frac{1}{2}$)

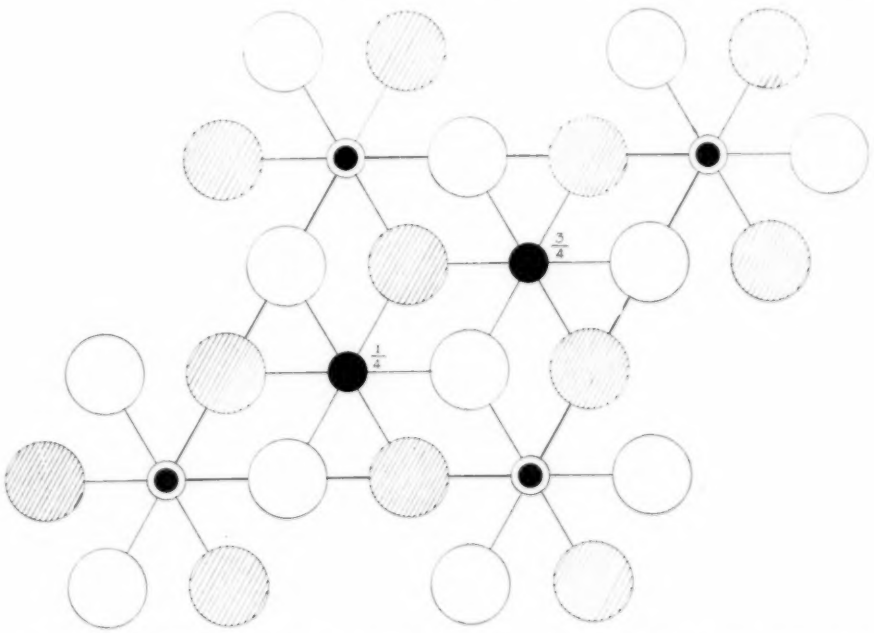

Fig. 1. Projection on the c-face of the structure of $LiIO_3$. The large circles represent oxygens at height 0. The large shaded circles represent oxygens at height $c/2$. The small solid circles represent iodine. The small solid centered circles represent lithium at height $c/4, 3c/4$.

with $u = 1/3$. The intensities calculated on the basis of this structure agree well with the observed ones, as will be seen from the tables.

Discussion of the Structure

In Fig. 1 is given a projection of the basal plane. The arrangement is a typical coordination lattice, of the hexagonal closed packed type met with in so many cases.

Almost perfect octahedra of oxygen atoms surround the iodine and lithium atoms. The IO_6-octahedra share only corners with each other. Sharing of the octahedral edges occur between IO_6 and LiO_6-polyhedra; while the LiO_6-octahedra share faces with each other. This result is in perfect agree-

ment with what one should expect: The higher charges the central cations have, the fewer are the number of shared corners between two polyhedra.

Although the lithium positions have not been determined from intensity considerations, there is not much doubt about the positions assigned to these atoms. In $LiNO_3$, where Li also lies inside an octahedron of oxygens, it was found that the lithium to oxygen distance = 2.15A. In $LiIO_3$ the lithium to oxygen distance is 2.23A.

The distance iodine to oxygen is also 2.23A. For comparison the iodine to oxygen distance in other crystals of the same coordination number is given. $KIO_3 - 2.23A$; $RbIO_3 - 2.26A$, $CsIO_3 - 2.33A$.

The shortest oxygen to oxygen distance is 3.16A. In a previous paper by W. H. Zachariasen[2] it was shown that groups $(XO_3)^{-n}$ have an unsymmetrical structure if $v = 3\times 8+2$ (v being the total number of valence electrons in the group). In the (IO_6) group there are $50 = 6\times 8+2$ electrons. So that from reasons of analogy it would not be astonishing to find asymmetry in the IO_6 group. This asymmetry probably would result in a slight displacement of iodine away from the center of the octahedron in the direction of one face. However no observations pointing in that direction were observed. The possibility of detecting very small displacements is only possible with extremely accurate intensity determinations.

Summary

Lithium iodate was examined by the oscillation and powder methods. The crystals were found to be hexagonal with 2 molecules in the cell $a = 5.469A \pm 0.003A$; $c = 5.155A \pm 0.005A$, $c/a = 0.9427$. The calculated density is 4.48.

The space group was found to be D_6^6 with 2 Li in (001/4) (003/4). 2 I in (1/3 2/3 1/4) (2/3 1/3 3/4) and 6 O in $(uu0)$ $(0\bar{u}0)$ $(\bar{u}00)$ $(\bar{u}\bar{u}\frac{1}{2})$ $(0u\frac{1}{2})$ $(u0\frac{1}{2})$ with $u = 1/3$.

The structure is based on the hexagonal closest packing. The lithium and the iodine atoms are both lying within oxygen octahedra. The distances Li-O and I-O are both 2.23A[3]. 2 lithium octahedra share faces with each other, one lithium and one iodine octahedra share only edges, two iodine octahedra only corners.

[2] W. H. Zachariasen, Phys. Rev. **37**, 775 (1931).

[3] It is probably that a value of u slightly less than 1/3 is more correct, say $u = 0.314$ which gives Li -0 2.15A and I $-0 = 2.28A$.

THE APPLICATION OF THE GEIGER-MÜLLER ION COUNTER TO THE STUDY OF THE SPACE DISTRIBUTION OF X-RAY PHOTOELECTRONS

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(Received May 4, 1931)

Abstract

The photographic plate in the apparatus for the magnetic analysis of x-ray photoelectrons has been replaced by a Geiger-Müller ion counter and the magnetic spectrum of the photoelectrons ejected from a thin film of gold by primary x-ray from molybdenum has been studied. Very great resolving power is obtained and considerable precision in determining the exact position of the lines (i.e. the energies of the photoelectrons). The numbers of L_{III} electrons of gold ejected by the $K\alpha_1$ x-ray of molybdenum have been plotted as a function of the angle of ejection and compared with the theoretical longitudinal distribution predicted by Schur.

Introduction

In the past many investigators[1] have observed the space distribution of x-ray photoelectrons in cloud expansion chambers. This method is powerful because one may observe directly the path taken by an individual photoelectron after ejection from the parent atom. In actual practice, however, the method has several shortcomings,[2] one of which is that except in a very few special cases the electrons coming from one level of the parent atom cannot be differentiated from those coming from another level.[3]

The method developed by one of the writers[4] enabled the longitudinal distribution of the photoelectrons to be studied as a function of both the energy of the incident photons and the level from which the electrons are ejected. While the change in relative intensities of "lines" in the "magnetic spectra" taken at various angles by this method yielded valuable information, the actual longitudinal distribution of a given group of photoelectrons could be obtained only qualitatively, because the photoelectrons were recorded photographically. With the aim of obtaining distribution curves of a more accurate nature, a new magnetic spectrograph has been constructed, in which the photographic plate has been replaced by a small Geiger-Müller tube.[5]

Apparatus

In Fig. 1 is shown the horizontal section through the centers of the slits of the new spectrograph. The photoelectrons are ejected from an exceedingly

[1] For a bibliography of work in this field see, e.g., Watson and Van den Akker, Proc. Roy. Soc. **A126,** 138 (1929).

[2] Williams, Nuttal and Barlow, Proc. Roy. Soc. **A121,** 611 (1928).

[3] Watson and Van den Akker, reference 1.

[4] Watson, Phys. Rev. **30,** 479 (1927).

[5] For a bibliography of work done on this extremely sensitive detector of ions see, e.g., Van den Akker, Rev. Sci. Instr. **1,** 672 (1930).

thin film of the element studied, which is deposited on a strip of celluloid 2 mm wide. This strip is supported with its length vertical, and so arranged at the axis of rotation of the apparatus that the electrons always leave the film normally to its surface. The width of the x-ray beam at the axis of rotation is about 4 mm, so that the film is included in the beam at all angular settings of the spectrograph. Each of the slits shown is 1/64 inch wide and 1/4 inch long. The slits S_1 and S_2 are 3 inches apart, and thus ρ, the radius of curvature of the electron orbits, is fixed at 1.5 inches. The slit S_3 and the windows W_2 and W_3 in the Geiger-Muller tube aid in setting the angular dial shown in Fig. 2. Once this setting has been made, the Geiger-Muller tube is shifted to a new position, axis at O', where the entrance window W_1 is more directly behind S_2.

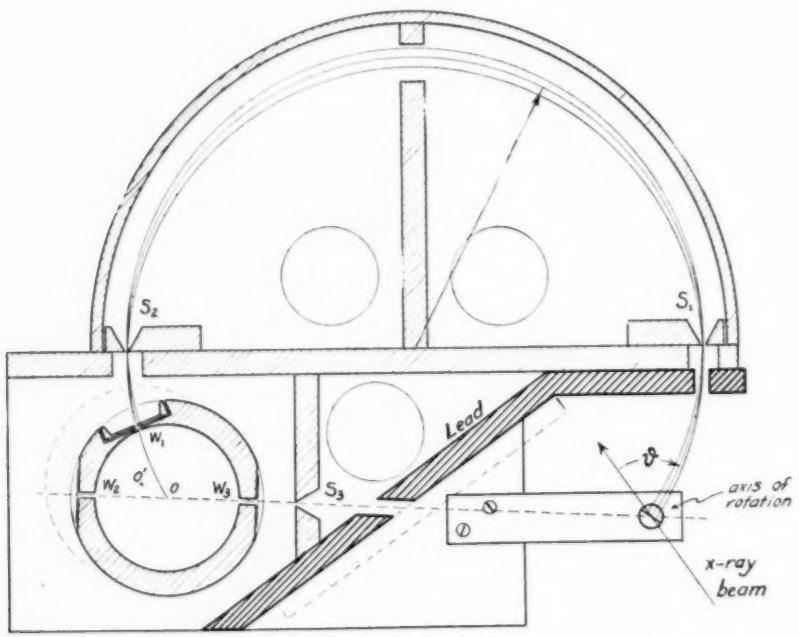

Fig. 1. Horizontal section of apparatus, showing arrangement of slits.

Rotation of the spectrograph from outside the chamber may be accomplished by means of a large brass taper, which is shown in Fig. 2. The lead-in B is a small brass pipe which connects the chamber of the Geiger-Müller tube to a gas system, while A is an electrical lead-in to the anode wire of the tube. A pointer fastened to the top of the taper enables one to read θ, the angle between the x-ray beam and the initial direction of the photoelectrons which enter S_1.

The entrance window W_1 is a set of five holes, each of 0.8 mm diameter, and arranged in a vertical line. A small disk fits into the wall of the tube, and this disk possesses five holes which fall over the five holes in the wall of the tube. This is shown in Fig. 3, in which is given a cross section of a tube of design later than that of the tube depicted in Fig. 2. A film of celluloid of the

order of 10^{-6} cm thick covers the holes of the small disk. This film must satisfy two requirements: It must be sufficiently thin to pass an appreciable fraction of the slowest photoelectrons, and yet it must be sufficiently strong to withstand the difference in pressure which exists between the interior and exterior of the tube (approximately 5 cm of mercury).

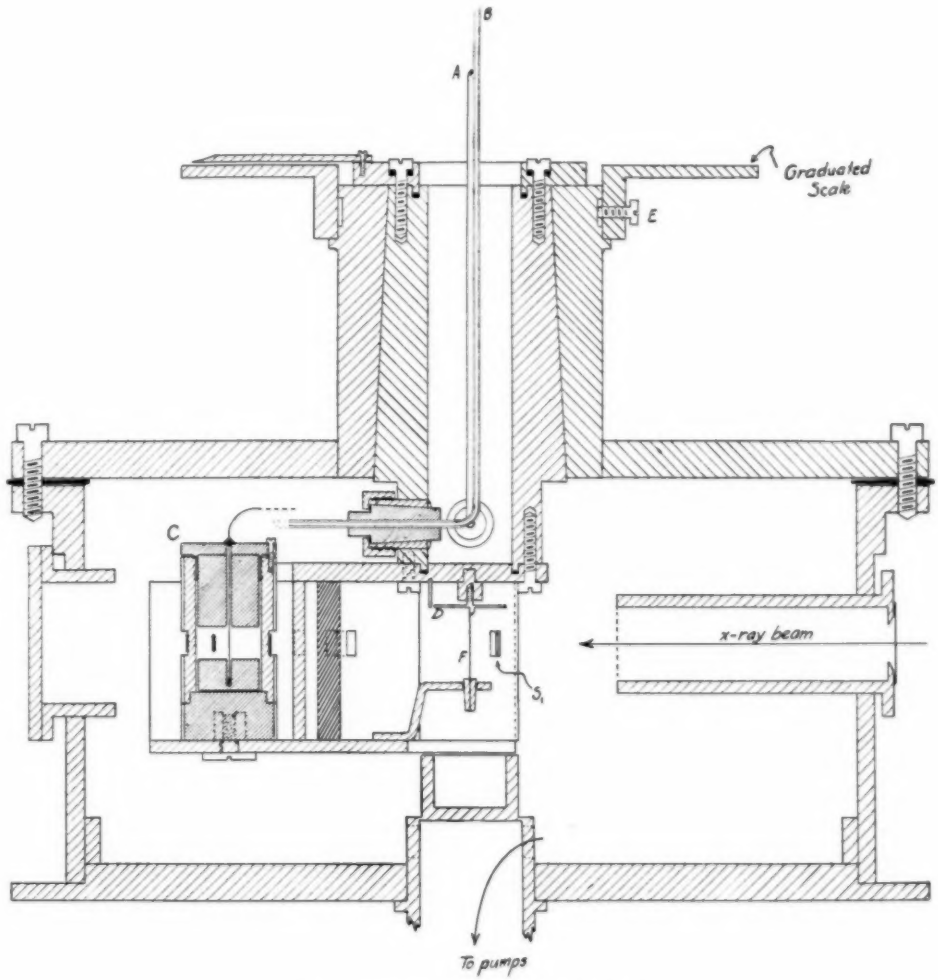

Fig. 2. Vertical section of apparatus.

A description of the specialized form of Geiger-Müller tube used in this research and of its operation has been given elsewhere.[6] The most important detail is the limitation of the active volume by the use of hard rubber plugs. This limitation of volume results in a very low "residual count;" and, when the anode wire is satisfactory, the electron count is independent of the potential of the anode over a range of about 50 volts. (When the whole of the

[6] Van den Akker, Rev. Sci. Instr. **1**, 672 (1930).

volume of the chamber is active the effect of the ends of the tube is to make the residual count a function of the potential of the anode).

The wiring diagram for the Geiger-Müller tube is given in Fig. 4. The tube is earthed, while the anode is connected to a source of high potential through

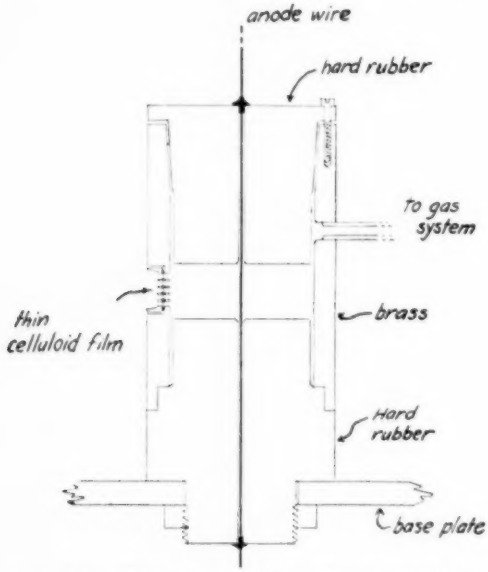

Fig. 3. Diagram of small electron counter, showing limitation of active volume by means of solid hard rubber plugs.

a resistance of 5×10^9 ohms. Since the spectrograph is placed at the center of a long, vertical solenoid, the connector between the anode and the amplifier

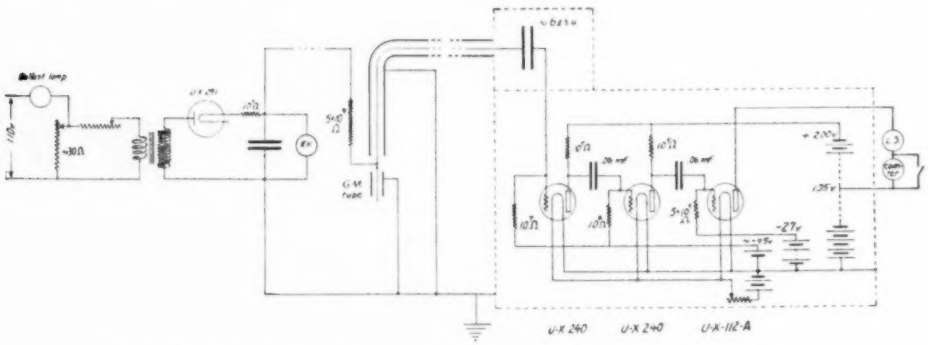

Fig. 4. General scheme of electrical connections for the Geiger-Müller tube.

is necessarily long. The strong electrical disturbances which come from the x-ray outfit make it necessary to shield this connector carefully; to satisfy this requirement, and an additional restriction on the total capacity to earth of the connector, the shielded connector is a very fine wire strung through a large lead pipe.

The results given in this paper were obtained when the x-rays were the primary rays of molybdenum, generated in a water-cooled Coolidge tube

driven at 30 kv and 20 m.a., and the electrons were ejected from a barely visible sputtered film of gold.

The Nature of the Magnetic Spectra

The results of two exploratory runs at $\theta = 80°$ are given in Figs. 5 and 6. In Fig. 5 is shown a small part of the whole spectrum which includes the double peak due to L_{III} electrons ejected from gold by Mo$K\alpha_{1,2}$. In each

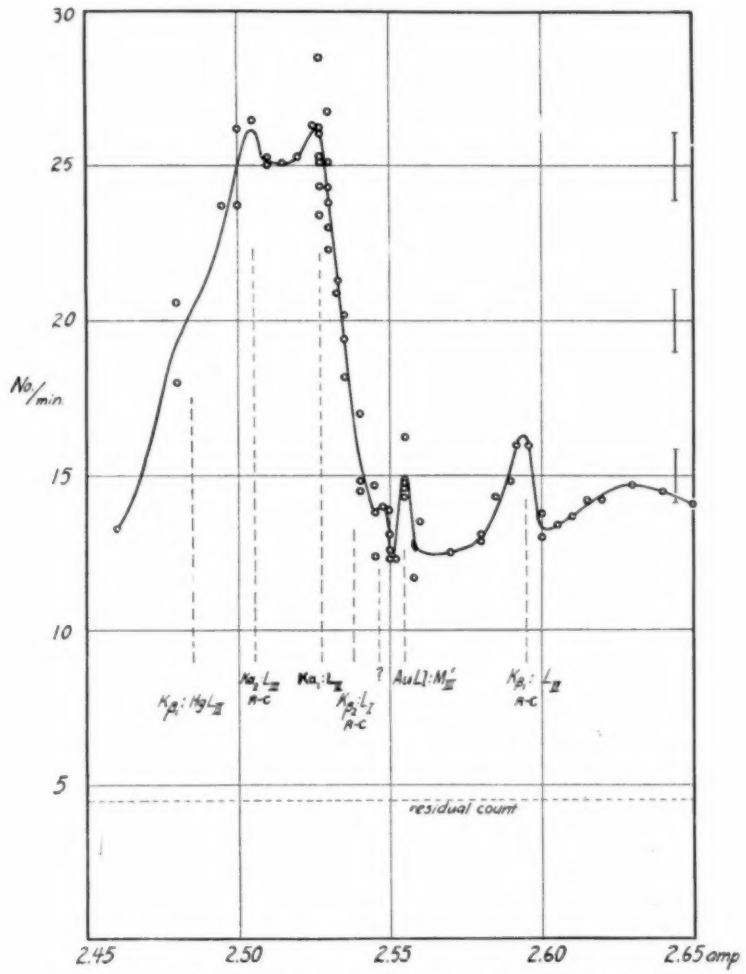

Fig. 5. A small part of the electron "spectrum" taken at 80°, showing the double peak due to L_{III} electrons of gold ejected by Mo$K\alpha_{1,2}$.

figure the number of impulses occurring in the Geiger-Müller tube per minute is plotted against the solenoid current. The spectrograph was calibrated with respect to the position of the $K\alpha_1 : L_{III}$ peak, the $H\rho$ value being that given by Robinson and Cassie.[7] All other positions indicated by vertical dashed lines were calculated. Where the precision measurements made by Robinson and

[7] Robinson and Cassie, Proc. Roy. Soc. **A113,** 282 (1928).

Cassie have been used, the letters "R–C" have been appended. In the calculation of the remaining positions, level values given in Vol. XXI of the Handbuch fur Physik were used. In all cases the ν/R values of the emission lines of molybdenum and gold and the values of the fundamental constants were those selected by Robinson and Cassie.

The sharpness of the peaks in Fig. 5 indicates good resolution, and shows that few electrons lost appreciable energy in getting out of the sputtered film. Each point shown was obtained by a ten minute period of counting, and hence the probable error for each point was not small, being one electron per minute for points in the neighborhood of 25 per minute. The heavy vertical dashes at the extreme right of Figs. 5 and 6 represent twice the probable error of individual points. The probable error of the curves drawn is in general

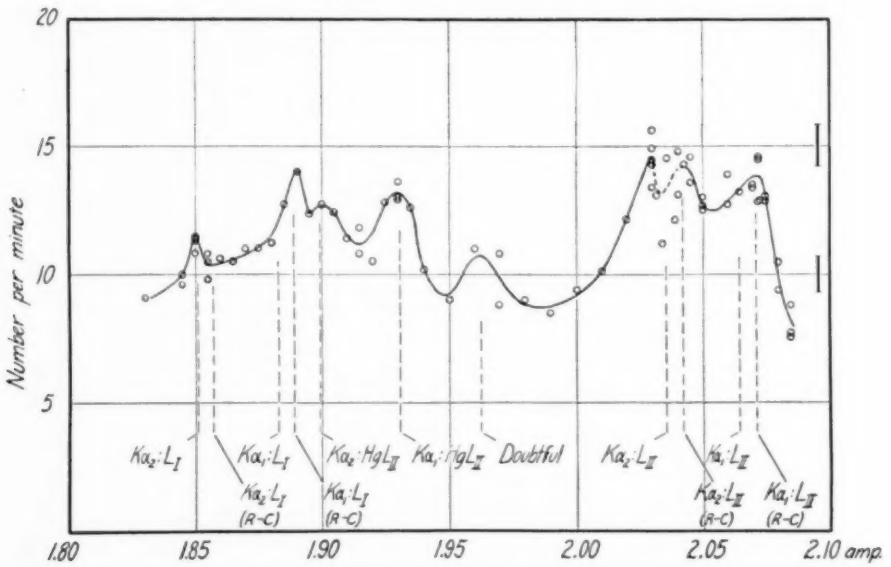

Fig. 6. The low velocity end of the electron "spectrum" showing peaks due to electrons from the L_{I} and L_{II} levels of gold.

somewhat smaller, being as small as 0.4 electrons per minute at certain points. The count obtained at zero magnetic field, the "residual count," was about 4.5 per minute. This count was not noticeably changed when the source of x-rays was cut off, showing that the effect of scattered x-rays was negligible.

The small peak at 2.555 amp can be attributed to electrons ejected from the M_{III} levels of gold atoms in which the transition ($M_{\text{I}} \rightarrow L_{\text{III}}$) may occur. Thus, while the M_{III} level in the normal gold atom has the value $\nu/R = 202.8$, the value of this level in an atom in which the above transition may occur is 206.7. The two peaks at 1.900 and 1.930 could not be attributed to electrons coming from gold. The sputtered film of gold had been exposed to mercury vapor at room temperature, however, and hence one might reasonably expect to find peaks due to electrons from mercury. The calculated positions of electrons ejected from the mercury L_{II} level by Mo$K\alpha_{1,2}$ were, respectively, 1.931 and 1.899 amp.

The Longitudinal Distribution of the L_{III} Electrons

In an attempt to measure the longitudinal distribution of electrons ejected from the L_{III} level of the gold atom by $K\alpha_1$, the $K\alpha_{1,2}$: L_{III} peaks were obtained at various angles. The difference between the ordinate of the peak at 2.528 amp and the ordinate of the valley at 2.551 amp was taken as a measure of the number of electrons ejected from the L_{III} level. This difference is plotted against the angle of ejection, θ, in Fig. 7. The deviation of the experimental curve from the points at 60° and 80° is a correction due to the loss of $K\alpha$ rays in passing through the celluloid strip which supported the sputtered film. This correction is negligible for all angles excepting those slightly less than 90°. It should be noted that this correction is not accurately known, and that an error in this correction will shift the maximum of the experimental curve through several degrees.

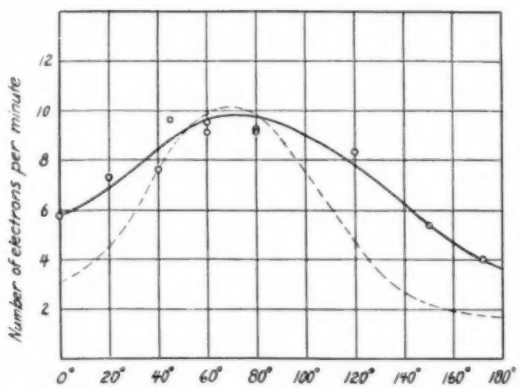

Fig. 7. The longitudinal distribution of L_{III} electrons of gold ejected by Mo$K\alpha_1$.

Schur[8] has recently given a theoretical expression for the longitudinal distribution of the L electrons taken collectively. This expression is divided into two parts, one giving the distribution of the L_I electrons, and the other giving the distribution of the L_{II} and L_{III} electrons combined. The latter part is

$$J(\theta,\phi) \sim \left\{1 + \frac{8I_L}{h\nu}\sin^2\theta\cos^2\phi + \frac{2v}{c}\cos\theta\left[1 + 2\left(1 + \frac{11I_L}{h\nu}\right)\sin^2\theta\cos^2\phi\right]\right\}$$

where $J(\theta, \phi)$ is the probability per unit solid angle that an electron will leave the parent atom in a direction making an angle θ with the forward direction of the x-ray beam, and the angle ϕ with the direction of the electric vector, ϕ being measured in a plane perpendicular to the beam of x-rays. The quantities I_L, ν, and v are respectively the mean energy of binding of the L_{II} and L_{III} electrons, the frequency of the incident radiation, and the speed of ejection of the photoelectrons. Since unpolarized rays were used, we integrate with respect to ϕ from 0 to π, and obtain

[8] Schur, Ann. d. Physik **4**, 433 (1930).

$$P(\theta) \sim \left\{1 + \frac{4I_L}{h\nu}\sin^2\theta + \frac{2v}{c}\cos\theta\left[1 + \left(1 + \frac{11I_L}{h\nu}\right)\sin^2\theta\right]\right\}.$$

This function is represented in Fig. 7 by the dashed curve. The wide departure of the experimental curve from the theoretical at small and large angles can be explained in part by nuclear scattering of the electrons in the sputtered film. Scattering can not explain the larger part of this departure, however, as spectra obtained in the past[9] reveal the important fact that certain lines, strong at 80°, fall to nearly zero intensity at 0°. On the other hand, the theoretical distribution is that of the L_{II} and L_{III} electrons combined, and it may be that the distribution of the L_{II} electrons is less isotropic than that of the L_{III} electrons. The maxima of the curves are both well forward of 90°, being at about 70°, and the ratio of the ordinates at 0° and 180° of the experimental curve is nearly the same as that of the theoretical curve. The experimental value of this ratio is 1.60, while Schur's function gives

$$P(0)/P(\pi) = (1 + 2v/c)/(1 - 2v/c) = 1.82.$$

[9] Watson and Van den Akker, reference 1.

ON THE PROBLEM OF THE ENTROPY OF THE UNIVERSE AS A WHOLE

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Abstract

The well-known problem of the entropy of the universe as a whole arises from the difficulties encountered by classical thermodynamics—first in failing to account for the presumed fact that the entropy of the universe has always been increasing at an enormous rate and nevertheless has not yet reached its maximum value—and second in failing to allow an emotionally satisfactory feeling towards our universe whose ultimate fate would be the stagnation of "heat-death." The purpose of the present article is to examine this problem from the point of view of the extension of thermodynamics to general relativity which has previously been made by the author.

A number of earlier contributions to the solution of the problem, which have been made from the standpoint of classical thermodynamics or statistical mechanics, are first briefly described in order to emphasize the very different character of the contribution to the problem made in the present article. It is then pointed out that the problem of the entropy of the universe arises in the classical thermodynamics because of the presumption that thermodynamic processes cannot take place both reversibly and at a finite rate, and that the general nature of the contribution to the problem offered by relativistic thermodynamics consists in showing the possibility of thermodynamic changes which could take place at a finite rate and at the same time reversibly without increase in entropy.

The principles of relativistic thermodynamics are then reviewed, and this difference between the classical and relativistic thermodynamics is shown by considering the possibilities of carrying out reversible changes at a finite rate in the properties of a thermodynamic fluid. In the classical thermodynamics it is found that no change in the thermodynamic properties could be allowed to take place at a finite rate, the entropy density of the fluid necessarily remaining constant in accordance with the equation

$$\frac{d\phi_0}{dt} = 0.$$

On the other hand, in relativistic thermodynamics it is found possible to allow changes to take place at a finite rate in the proper volume of the fluid, due to changes in the gravitational potentials $g_{\mu\nu}$, and still maintain reversibility provided the changes satisfy the relation

$$\frac{\partial}{\partial x_4}\left(\phi_0\sqrt{-g}\frac{dx_4}{ds}\right) = 0.$$

To exhibit the nature of the reversible changes at a finite rate thus permitted in relativistic thermodynamics, consideration is given to the highly idealized model of a non-static universe filled with black-body radiation as a thermodynamic fluid, and it is shown that the radius, total proper volume, and entropy density of such a universe could be changing at a finite rate and yet reversibly without increase in entropy. Furthermore, in the case of an expanding model of the kind considered, it is shown that an ordinary observer, who marks out with rigid meter sticks a small region of

this universe in his immediate vicinity for study, would find the energy density, energy content, and the temperature of this region decreasing with the time, and would find the number of quanta leaving the region per second greater than the number entering, and the average frequency of the quanta that leave greater than that of those that return. These phenomena would be interpreted by the observer, from a classical point of view, as due to radiation from his neighborhood into the colder surroundings of space and hence as leading to an increase in entropy, in spite of the fact that all the processes taking place in such a model would actually be reversible from the point of view of the relativistic thermodynamics which should be applied to such a problem.

In conclusion remarks are made concerning the disparity between the above model, which was chosen for purposes of illustration because of its mathematical simplicity, and models which would be more suitable to serve as representations of the actual universe. And some indication is given of the further developments that should be undertaken.

PART I. INTRODUCTION

§1. Purpose of present article.

IN A number of previous articles I have endeavored to present the principles for an extension of thermodynamics to general relativity[1] and to consider some of the applications of the new system of relativistic thermodynamics based on these principles.[2] The purpose of the present article is to examine the bearings of relativistic thermodynamics on the well-known problem of the entropy of the universe as a whole. It will be found that this extended thermodynamics provides new possibilities for thermodynamic processes to take place at a finite rate without increase in entropy. And it will be shown that the recognition of these new possibilities not only appears to be essential for a true understanding of the problem of the entropy of the universe, but may even provide to a greater or lesser extent the basis for its solution.

§2. The nature of the problem of the entropy of the universe.

In accordance with the views of the classical thermodynamics all thermodynamic processes, actually taking place in the universe at a finite rate, were regarded as accompanied by an increase in entropy. Among these processes appeared a wide variety of immediately appreciated terrestial occurrences of a meteorological, biological or technological nature in which the increase of entropy depended for the most part on the degradation of energy originally received as radiation from the sun,—in addition, various tidal actions in which the increase of entropy resulted from the degradation into heat of mechanical energy of astronomical motions;—and quantitatively most important of all, the continuous flow of radiation from the stars with a great increase in entropy due to the presumable drop in temperature in passing from the hot interior of the stars to the cold depths of intergalactic space.

In general the view was held that entropy was everywhere increasing at an enormous rate and that this would continue until the entropy of the universe

[1] Tolman, Proc. Nat. Acad. **14,** 268 (1928); ibid. **14,** 701 (1928); Phys. Rev. **35,** 875 (1930); ibid. **35,** 896 (1930).

[2] Tolman, Proc. Nat. Acad. **14,** 348 (1928); ibid. **14,** 353 (1928); ibid. **17,** 153 (1931); Phys. Rev. **35,** 904 (1930); Tolman and Ehrenfest, Phys. Rev. **36,** 1791 (1930).

had reached its maximum,—the sun and stars cold, all of creation dead and unchanging.

Such a view, however, carries with it two difficulties. The first difficulty has genuine intellectual validity and can be expressed by the question: Why has not the entropy of the universe already reached its maximum value in the infinite past time which has presumably been available? The second difficulty has perhaps only emotional validity and can be expressed by the question: What significance can we ascribe to a universe whose ultimate fate is merely the "heat-death" of maximum entropy? These are the difficulties which constitute the problem of the entropy of the universe.

§3. Nature of earlier contributions to the solution of the problem.

Various suggestions have been made with regard to the solution of the problem. It will be profitable to consider some of them briefly in order to emphasize the very different nature of the suggestion which will be made in this article.

a. Finite time since creation. The most obvious treatment of the problem is to assume that the universe was indeed created at a finite time in the past with sufficient available energy so that the entropy has not yet reached its maximum value. In the future this maximum would be reached and all significant changes would cease. A modification of the treatment could be made by assuming an infinite past during which the universe was in a quiescent metastable state of large available energy, and a disturbance at a finite time in the past which initiated the process of degradation.

These suggestions depend too greatly on special *ad hoc* assumptions to be scientifically satisfying.

b. Continuous regeneration. A second type of suggestion depends on the assumption of the existence of regenerative processes of such a nature as to maintain the universe in an approximately steady condition. Thus Millikan[3] has suggested the four-step cycle: (1) Matter in the stars is transformed into radiation which flows out into intergalactic space; (2) the radiation in intergalactic space is transformed into electrons and protons; (3) the electrons and protons combine to form helium and other elements, giving rise to the production of the observed cosmic rays; (4) the matter thus formed drifts back into the stars, thus completing the cycle. The evidence for step (2) is completely lacking at present; steps (2) and (3) assume the occurrence of processes of synthesis under the theoretically unfavorable conditions of extremely low concentration; and the cycle contradicts the principle of microscopic reversibility.[4] The evidence for step (1), however, is very strong, the evidence for step (3) cannot be dismissed as trivial, and there is no inherent improbability in step (4).

c. Continuous approach to maximum entropy. A third type of suggestion

[3] Millikan and Cameron, Proc. Nat. Acad. **14,** 637 (1928).

[4] For a partial historical account of this principle, see Tolman, Proc. Nat. Acad. **11,** 436 (1925). For a discussion of the principle, see for example Tolman, "Statistical Mechanics" Chap. 15, Chemical Catalog Co., New York, 1927.

would be to assume an infinite past for the universe, coupled with ever decreasing values for the entropy of the universe as we examine backwards in the past and a continuous asymptotic approach to the maximum of entropy in the future.[5] If such an assumption were allowable, it would avoid the difficulty of a limited past time for the existence of the universe, but the difficulties of a practical exhaustion of the energy available for human needs within a finite time in the future would not appear to be avoided. The assumption would perhaps not be a possible one for a finite universe of finite energy content, for which we have some evidence.

d. Fluctuations in entropy in accordance with its statistical-mechanical interpretation. A fourth of type of contribution to the problem depends on the statistical mechanical interpretation of entropy, as given most clearly by Boltzmann's famous *H*-theorem. In accordance with this theorem it is found that, although there is a great probability for the entropy of a system to increase when it has less than its maximum value, it is not certain that this will take place and fluctuations away from the maximum of entropy will occur. This furnishes the possibility that the universe has existed for an infinite time in the past and that we are now experiencing a return of the universe or of that portion which is within our range of observation towards a condition of maximum entropy after a major fluctuation away from that value.

This important possibility was clearly presented by Boltzmann[6] over thirty years ago. The enormous improbability of a major fluctuation of the kind assumed does not necessarily furnish a valid argument against the explanation, since, as pointed out to me in conversation by Mrs. Ehrenfest-Afanassjewa, the existence of sentient beings to observe the rare phenomenon could presumably only occur at the time of decay of such a fluctuation. From the point of view of human wishes, however, the explanation is not entirely satisfying, since it implies that man himself is a transitory and improbable phenomenon, that our surroundings are now headed with almost complete certainty towards a condition at least close to that of maximum entropy, and that the conditions under which life, as we know it, is possible are almost never present. Nevertheless, these objections have emotional rather than intellectual validity and the part played by the theory of statistical fluctuations in a relatively complete solution of the problem of the entropy of the universe may prove to be no mean one.

§4. Nature of the present contribution to the solution of the problem.

The present contribution to the problem of the entropy of the universe is based on the system of relativistic thermodynamics which I have developed. The general nature of the contribution depends on an extension given by this relativistic thermodynamics in our ideas as to the kind of processes which can occur at a finite rate without producing any increase in entropy.

As an illustration of this extension in our ideas, it would be impossible

[5] This possibility was suggested to me by some remarks of the late Professor William James which were told me in conversation by Professor Gilbert N. Lewis.

[6] Boltzmann, Wied. Ann. **60,** 392 (1897).

from the point of view of classical thermodynamics to carry out an actual expansion of a thermodynamic fluid reversibly and at a finite rate, since the friction of moving parts and the deficiency between the actual pressure exerted by the fluid and that which could be exerted with an infinitely slow rate of expansion would lead to an increase in entropy. Nevertheless, in relativistic thermodynamics we shall find that the *proper* volume associated with a thermodynamic fluid could increase at a finite rate, owing to a finite rate of change in the gravitational potentials $g_{\mu\nu}$, without involving any increase in entropy.

In further illustration, it appeared impossible in the classical thermodynamics for a flow of heat to take place reversibly and at a finite rate, owing to the increase in entropy connected with the finite temperature drop necessary to maintain the finite rate of flow. Nevertheless, in relativistic thermodynamics, we shall find that the reversible increase in proper volume, mentioned in the paragraph above, would make it possible for heat radiation to be regarded by an ordinary observer as flowing out of a given region of interest at a finite rate, without any increase in the entropy of the system as a whole.

It is evident from these examples, that relativistic thermodynamics increases in an important manner the variety of changes which could be taking place in a universe which is actually in a state of maximum entropy, and makes it necessary to re-examine processes which we have formerly taken as evidence that the entropy of our own universe is actually increasing at an enormous rate.

In Part II, we shall first consider the general bearing of relativistic thermodynamics on changes in thermodynamic condition without increase in entropy. In Part III, we shall then apply relativistic thermodynamics to the very special model of a non-static universe filled solely with radiation. Such a model ignores very characteristic features of the actual universe, but mathematically is relatively simple to handle and will present some features which appear analogous to phenomena in the actual universe. Finally in Part IV, we shall try to give some criticism of the role that the new ideas might play in the general solution of the problem of the entropy of the universe.

Part II. Relativistic Thermodynamics

§5. The first and second laws of relativistic thermodynamics.

The extension of thermodynamics to general relativity can be based on two principles which may be regarded as the relativistic generalization of the first and second laws of classical thermodynamics.

In accordance with the first of these principles, any thermodynamic process occurring in the universe must take place in such a way as to agree with the principles of relativistic mechanics as given by the tensor density equation

$$\frac{\partial \mathfrak{T}_{\mu}^{\nu}}{\partial x_{\nu}} - \frac{1}{2}\mathfrak{T}^{\alpha\beta}\frac{\partial g_{\alpha\beta}}{\partial x_{\mu}} = 0 \tag{1}$$

or the equivalent non-tensorial yet nevertheless covariant equation

$$\frac{\partial(\mathfrak{T}_\mu^\nu + \mathfrak{t}_\mu^\nu)}{\partial x_\nu} = 0 \tag{2}$$

where $\mathfrak{T}_\mu^\nu$ is the tensor density of material energy and momentum, $\mathfrak{t}_\mu^\nu$ the pseudo tensor density of potential energy and the $g_{\alpha\beta}$ the gravitational potentials.

Since these equations reduce to the ordinary energy-momentum principle in flat space-time where the gravitational field is negligible, the analogy of this first principle to the ordinary first law of thermodynamics is evident. In applying the principle to thermodynamic considerations, the system involved will of course be treated from a macroscopic point of view, and this is an advantage since the applicability of these equations to microscopic phenomena would certainly not be in accord with the development of quantum mechanics, which has taken place since their formulation.

The second principle of relativistic thermodynamics may be stated in the form

$$\frac{\partial}{\partial x_\mu}\left(\phi_0\sqrt{-g}\,\frac{dx_\mu}{ds}\right)dx_1dx_2dx_3dx_4 \geqq \frac{dQ_0}{T_0} \tag{3}$$

where ϕ_0 is the proper density of entropy as measured by a local observer, using Galilean coordinates which are at rest with respect to the mass motion of the thermodynamic fluid at the point of interest, the quantities dx_μ/ds are the macroscopic "velocities" of the fluid at the point of interest as measured in the coordinate system x_1, x_2, x_3, x_4, the quantity dQ_0 is the heat flowing through the boundary into the infinitesimal region *and* during the infinitesimal time, denoted by $dx_1dx_2dx_3dx_4$, as measured in proper coordinates, and T_0 the temperature of the boundary also measured in proper coordinates.

The justification for the principle lies in the fact that it has been shown to be a natural covariant generalization of the ordinary second law of thermodynamics valid in flat space-time, Eq. (3) being a tensor equation of rank zero which reduces in flat space-time and Galilean coordinates to

$$\left[\frac{\partial\phi}{\partial t} + \frac{\partial}{\partial x}(\phi u) + \frac{\partial}{\partial y}(\phi v) + \frac{\partial}{\partial z}(\phi w)\right]dxdydzdt \geqq \frac{dQ}{T} \tag{4}$$

where ϕ is the density of entropy, u, v and w are the component velocities of the fluid, dQ is the heat flowing into the region $dxdydz$ in the time dt, and T is the temperature, all these quantities now being measured in the particular set of Galilean coordinates x, y, z, t which is being used.

§6. Application of the relativistic second law to a finite adiabatic system.

Let us now apply our new form of the second law as given by Eq. (3) to a finite thermodynamic system, by taking x_1, x_2, x_3 as being the space-like coordinates and carrying out an integration over the spatial region of interest. If we carry out such an integration, using coordinates such that the limits

of integration necessary to include the system fall on the boundary which separates the system from its surroundings, it is evident that the summation of dQ_0/T_0 over the interior of the system will cancel out, since any heat entering a given element of volume is abstracted from neighboring elements. Hence dividing Eq. (3) by dx_4, writing out the separate terms corresponding to the different values of μ, and performing the integration we obtain, with some rearrangement in order,

$$\begin{aligned}\iiint \frac{\partial}{\partial x_4}\left(\phi_0\sqrt{-g}\,\frac{dx_4}{ds}\right)dx_1dx_2dx_3 \\ \geqq -\iiint\left[\frac{\partial}{\partial x_1}\left(\phi_0\sqrt{-g}\,\frac{dx_1}{ds}\right)+\frac{\partial}{\partial x_2}\left(\phi_0\sqrt{-g}\,\frac{dx_2}{ds}\right)\right. \\ \left.+\frac{\partial}{\partial x_3}\left(\phi_0\sqrt{-g}\,\frac{dx_3}{ds}\right)\right]dx_1dx_2dx_3+\sum\left(\frac{1}{T_0}\,\frac{dQ_0}{dx_4}\right)_{\text{BOUNDARY}}\end{aligned} \tag{5}$$

The last term on the right hand side of the above inequality is the total value of the quantity $(1/T_0)(dQ_0/dx_4)$ taken over the boundary which separates the system from its surroundings, and by performing the indicated integrations the other terms on the right hand side of the expression can also be seen to depend solely on conditions at the boundary. We obtain

$$\begin{aligned}\iiint \frac{\partial}{\partial x_4}\left(\phi_0\sqrt{-g}\,\frac{dx_4}{ds}\right)dx_1dx_2dx_3 \\ \geqq -\iint\left|\phi_0\sqrt{-g}\,\frac{dx_1}{ds}\right|_{x_1}^{x_1'}dx_2dx_3-\iint\left|\phi_0\sqrt{-g}\,\frac{dx_2}{ds}\right|_{x_2}^{x_2'}dx_1dx_3 \\ -\iint\left|\phi_0\sqrt{-g}\,\frac{dx_3}{ds}\right|_{x_3}^{x_3'}dx_1\,dx_2+\sum\left(\frac{1}{T_0}\,\frac{dQ_0}{dx_4}\right)_{\text{BOUNDARY}}\end{aligned} \tag{6}$$

where the limits of integration at the boundary are denoted by x_1, x_1' etc.

This expression (6) may be regarded as a general statement of the relativistic second law of thermodynamics as applied to finite systems. Defining the entropy of the system as

$$S=\iiint\left(\phi_0\sqrt{-g}\,\frac{dx_4}{ds}\right)dx_1dx_2dx_3 \tag{7}$$

it gives the relation which must hold between the rate at which the entropy of a finite system is changing with the time x_4 and those conditions at the boundary which determine the flux of matter and the flow of heat between the system and its surroundings.

For an adiabatic system with no flux of matter or flow of heat between the system and its surroundings we shall have the quantities dx_1/ds, dx_2/ds, dx_3/ds, and dQ_0/dx_4 equal to zero at the boundary and the expression will then reduce to

$$\frac{dS}{dx_4} = \iiint \frac{\partial}{\partial x_4}\left(\phi_0 \sqrt{-g}\, \frac{\partial x_4}{ds}\right) dx_1 dx_2 dx_3 \geqq 0. \tag{8}$$

In accordance with this expression the entropy of an adiabatic system cannot decrease with the time but can only increase or remain constant. As in the classical thermodynamics, adiabatic processes in which the entropy increases with the time may be called irreversible, since neglecting improbable fluctuations the system after such a process could not of itself return to the original state of lower entropy; while processes in which the entropy remains constant may be called reversible.

§7. Increased possibility for reversible processes in relativistic thermodynamics.

With the help of the foregoing considerations we may now compare the conditions which would be imposed by classical and by relativistic thermodynamics on the occurrence of reversible processes. In the present section we shall show that the new thermodynamics offers the possibility for a kind of thermodynamic change which was not contemplated in the classical thermodynamics, and which might take place at a finite rate without increase in entropy, in contrast to the conclusion of classical thermodynamics that reversible thermodynamic processes could not take place at a finite rate. And in later sections we shall show by a simple specific example that such reversible processes taking place at a finite rate might actually be realized, and play a possible part in cosmological happenings.

a. Classical treatment of entropy changes in a thermodynamic fluid. Let us first illustrate the kinds of classical considerations which have formerly lead to the conclusion that thermodynamic processes could not take place both reversibly and at a finite rate.[7] To do this we may consider the conditions which would be imposed by classical thermodynamics on reversible changes in the condition of a thermodynamic fluid.

In the classical thermodynamics we could evidently write for the entropy of a finite portion of thermodynamic fluid enclosed in a suitable container the expression

$$S = \iiint \phi\, dx dy dz \tag{9}$$

where ϕ is the density of entropy as measured in the particular set of (Galilean) coordinates x, y, z, t which the observer uses, and the integration is to be taken over the whole volume of the container.

If now we consider the possible reversible changes which could take place in this thermodynamic fluid, it is evident in the first place that we could permit no relative motion between different portions of the fluid, since the decay of this motion would lead to an increase in entropy, and we may hence

[7] Of course the classical thermodynamics permitted ideal *mechanical* processes to take place at a finite rate without increase in entropy, but the distinction between mechanical and thermodynamic processes was clear enough so that this did not prove to be a source of confusion.

use a set of coordinates in which the thermodynamic fluid as a whole would be at rest and rewrite our expression for the entropy in the form

$$S = \iiint \phi_0 \, dx dy dz \tag{10}$$

where ϕ_0 is the proper density of entropy. In the second place, it is evident that we could only permit adiabatic changes, since if we allowed heat flow in our system at a finite rate we should have increases in entropy arising from the finite temperature gradient which would be necessary to maintain this flow. Hence in accordance with the classical thermodynamics the condition for our contemplated process to be reversible would be that of constant entropy as given by the equation

$$\frac{d}{dt} \iiint \phi_0 \, dx dy dz = 0. \tag{11}$$

In the third place, it is evident that our process could not involve a change in volume at a finite rate, for example by the withdrawal of a piston, since this would involve mass flow of portions of the fluid which would lead to an increase in entropy that could be calculated from the difference between the pressure actually exerted by the fluid on the moving piston and that which would be exerted at an infinitesimally slow rate of expansion. Hence the condition given by Eq. (11) for our contemplated reversible process might now be rewritten with the differentiation inside the integral sign in the form

$$\iiint \frac{d\phi_0}{dt} \, dx dy dz = 0. \tag{12}$$

This final condition, moreover, could evidently be satisfied in our case only by taking

$$\frac{d\phi_0}{dt} = 0 \tag{13}$$

at all points of the fluid, since for a stationary fluid with no flow of heat there would be no possibility at any point for negative values of the quantity $d\phi_0/dt$.

This, however, completes the considerations necessary for the classical conclusion that there could be no thermodynamic change at all in our fluid which takes place both reversibly and at a finite rate. Indeed we see that no changes could take place in the system as a whole through interaction with its surroundings, since we have found that its volume could not be allowed to change at a finite rate and heat could not be allowed to flow through its boundary at a finite rate, and no changes could take place in the interior condition of the fluid since we have found that it could have no macroscopic internal motions, no internal flow of heat, and no changes in local entropy density which take place at a finite rate.

b. Relativistic treatment of entropy changes in a thermodynamic fluid. We

must now compare this conclusion with that which we would obtain by applying relativistic thermodynamics to the same system, namely a finite portion of thermodynamic fluid. In this case in accordance with expression (8) in the preceding section §6, the condition for a reversible adiabatic change in the condition of the fluid would be

$$\iiint \frac{\partial}{\partial x_4}\left(\phi_0 \sqrt{-g}\,\frac{dx_4}{ds}\right) dx_1 dx_2 dx_3 = 0 \tag{14}$$

where x_4 is the time like coordinate and the integration is to be taken over the whole range of spatial coordinates x_1, x_2, x_3 necessary to include the fluid. And this condition can evidently be satisfied if we have the equality holding at each point in the fluid

$$\frac{\partial}{\partial x_4}\left(\phi_0 \sqrt{-g}\,\frac{dx_4}{ds}\right) = 0 \tag{15a}$$

or

$$\frac{1}{\phi_0}\,\frac{\partial \phi_0}{\partial x_4} = -\,\frac{1}{\sqrt{-g}\,\dfrac{dx_4}{ds}}\,\frac{\partial}{\partial x_4}\left(\sqrt{-g}\,\frac{dx_4}{ds}\right). \tag{15b}$$

This expression gives a relation between the percentage rate at which the proper entropy density ϕ_0 is changing with the time x_4 at a given point and the percentage rate at which the quantity $(\sqrt{-g}\,dx_4/ds)$ is changing with the time at that same point. The value of this latter quantity, however, is determined by the gravitational field at the point in question, and by the kind of coordinate system $x_1 \cdots x_4$ which is being used.

If now we assumed the gravitational field negligible, as is tacitly done in the classical thermodynamics, and had a fluid with no relative motion between its parts, we could choose a system of Galilean coordinates x, y, z, t in which the fluid as a whole would be at rest. In this system of coordinates the quantities $\sqrt{-g}$ and dx_4/ds would have the constant value unity and the condition given by Eqs. (15) would reduce to the result

$$\frac{d\phi_0}{dt} = 0 \tag{16}$$

which we have already found to be characteristic of the classical thermodynamics. It is thus by a neglect of the gravitational field and its possible change with time that the classical thermodynamics has been led to the conclusion that no reversible processes can occur at a finite rate.

On the other hand in relativistic thermodynamics we must not assume that the gravitational field is necessarily negligible but must specifically consider the part which it plays in thermodynamic processes. Hence in relativistic thermodynamics we must consider the condition for reversibility given by Eq. (15) in its full form, and retain the possibility of mutual changes in gravitational field and entropy density taking place together at a finite rate in such a way as to satisfy this condition for reversibility.

In Part III we shall consider a definite model which exhibits such a mutual change in gravitational field and entropy density taking place at a finite rate and satisfying the condition for reversibility. To conclude the present section, however, we may first investigate somewhat further the general nature of the reversibility requirement given by Eq. (15).

Consider the case of a thermodynamic fluid which is at rest with respect to the spatial coordinates x_1, x_2, x_3 which are being used. Since the macroscopic velocities dx_1/ds, dx_2/ds, and dx_3/ds are everywhere zero by hypothesis, it is evident that the amount of fluid in any given coordinate range $dx_1dx_2dx_3$ would not be changing with the time since there is no flow across the boundary. In accordance with the principles of relativity, however, we can then write for the proper volume dV_0 of the small element of fluid in such a coordinate range the well-known equation

$$dV_0 = \sqrt{-g}\, dx_1dx_2dx_3 \frac{dx_4}{ds} \tag{17}$$

and substituting this expression into the condition for reversibility, as given by Eq. (15a), we can rewrite this condition in the new form

$$\frac{\partial}{\partial x_4}\left(\phi_0\sqrt{-g}\, dx_1dx_2dx_3 \frac{dx_4}{ds}\right) = \frac{\partial}{\partial x_4}(\phi_0\, dV_0) = 0 \tag{18}$$

since the coordinates x_1, x_2 and x_3 are independent of the coordinate x_4.

This equation, however, states that the total entropy for each given small element of fluid shall be constant as measured by a local observer, and this is merely the condition for a change in the proper volume of the element with no flow of heat and with balance between internal and external pressures. Hence if we had a fluid with no flow of heat and constant proper pressure throughout, a finite rate of alteration in the gravitational field which produced no flow of heat and changed the proper pressure at the same rate throughout the fluid would satisfy the condition of reversibility. This alteration in gravitational field, however, would lead to an alteration in proper volume and thus to alteration in the entropy density, so that the thermodynamic state of the fluid would be changing reversibly and at a finite rate. It is this dependence of proper volume on gravitational field, which was quite outside of the considerations of the classical thermodynamics, which leads in relativistic thermodynamics to the possibility of reversible processes which take place at a finite rate.

Part III. Application to a Specific Model

§8. The general nature of the model.

We may now apply the foregoing considerations to a specific model. For this purpose we shall take a non-static universe[8] filled with a uniform density of black-body radiation. The choice of this model is not made because it is

[8] For an account of various treatments which have been given to the non-static line element for the universe, see Tolman, Proc. Nat. Acad. **16,** 582 (1930).

thought to give a close approximation to the actual state of the universe but because the mathematical treatment will be relatively simple. The model neglects the presence of matter and its agglomeration into stellar systems which are very characteristic features of the actual universe. Nevertheless, we shall find that the behaviour of the radiation in such a universe furnishes a surprizing possibility of insight into the flow of radiation from the stars which is such a puzzling feature of the actual universe.

§9. The line element for the non-static universe.

The line element for a non-static universe filled with a uniform distribution of matter and energy can be derived[9] by treating the contents of the universe for the purposes of large-scale considerations as though filled with a perfect fluid, on the basis of the two requirements, (a) that the fluid shall at all times be uniformly distributed spatially, and (b) that particles (nebulae) which are stationary in the coordinate system used shall fulfill the stability requirement of not being subject to acceleration.

The line element so obtained can be written in a variety of forms depending on the choice of coordinates, and for the purpose of the discussions in the present article it will be most convenient to write it in the form[10]

$$ds^2 = -e^{g(t)}\left(\frac{dr^2}{1 - r^2/R^2} + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2\right) + dt^2 \tag{19}$$

where r, θ and ϕ are the spatial coordinates, t is the time coordinate, R is a constant, and the dependence of the line element on the time is given by the exponent $g(t)$.

§10. Certain general properties of the non-static universe.

Before proceeding to our special model, it will be desirable to recall certain properties which are implied in general for the non-static universe by the form of the line element and which will be needed in our later discussion.

In accordance with the requirement (a) on which the line element was derived, the proper macroscopic density ρ_{00} and the proper pressure p_0 of the fluid which fills the universe will be independent of the position r, θ, ϕ, but may be changing with the time t. And indeed working out the components of the energy-momentum tensor T_μ^ν which correspond to the line element (19) and equating to those for a perfect fluid we obtain as the only non-vanishing components[11]

$$8\pi T_1^1 = 8\pi T_2^2 = 8\pi T_3^3 = -8\pi p_0 = \frac{1}{R^2}e^{-g} + \ddot{g} + \frac{3}{4}\dot{g}^2 - \Lambda \tag{20}$$

$$8\pi T_4^4 = 8\pi\rho_{00} = \frac{3}{R^2}e^{-g} + \frac{3}{4}\dot{g}^2 - \Lambda \tag{21}$$

[9] Tolman, Proc. Nat. Acad. **16,** 320 (1930). See also Ibid. **16,** 409 (1930), and note that the five assumptions mentioned in §2 of that article can be included under the heading of the two requirements (a) and (b) given above.

[10] Tolman, Proc. Nat. Acad. **16,** 511 (1930). Eq. (5). Note that the $\bar{r}$ of that article is our present r.

[11] Tolman, Proc. Nat. Acad. **16,** 409 (1930). Eq. (2).

where Λ is the cosmological constant; and these equations give the dependence of pressure and density on the exponent g and its time derivatives $\dot{g}$ and $\ddot{g}$, and thus on the time itself.

With the help of these expressions for the components of the energy-momentum tensor we can now easily apply the principles of relativistic mechanics in the well-known form

$$\frac{\partial \mathfrak{T}_{\mu}^{\nu}}{\partial x_{\nu}} - \frac{1}{2}\mathfrak{T}^{\alpha\beta}\frac{\partial g_{\alpha\beta}}{\partial x_{\mu}} = 0. \tag{22}$$

With $\mu = 1, 2, 3$ we merely obtain identities, but substituting into this equation for the case $\mu = 4$ we can easily obtain after dividing through by a constant factor[12]

$$\frac{d}{dt}(\rho_{00}\, e^{3g/2}) + p_0 \frac{d}{dt} e^{3g/2} = 0. \tag{23}$$

This important result can evidently also be obtained directly by combining Eqs. (20) and (21).

In accordance with the requirement (b) on which the line element was derived, particles which are at rest with respect to the coordinate system r, θ, ϕ will not be subject to acceleration but will remain at rest. And this can be directly verified by calculating the Christoffel three-index symbols which correspond to the line element (19) and substituting in the geodesic equation which governs the motions of particles in general relativity.

As a result of the foregoing, observers who are at rest with respect to the coordinate system will remain permanently so. And in accordance with the form of the line element (19), for such observers, the proper time as measured by local clocks will evidently agree with the coordinate time t. On the other hand, for the proper distance dl_0 as measured with rigid meter sticks we shall evidently have

$$dl_0 = \frac{e^{g/2}dr}{\sqrt{1 - r^2/R^2}} \tag{24}$$

for points at the coordinate distance dr in the radial direction, and

$$dl_0 = re^{g/2}d\theta \quad \text{and} \quad dl_0 = r\sin\theta e^{g/2}d\phi \tag{25}$$

for the θ and ϕ directions. For the proper volume dV_0 associated with a given small range of coordinates we shall have

$$dV_0 = \frac{r^2 \sin\theta\, e^{3g/2}}{\sqrt{1 - r^2/R^2}} dr d\theta d\phi. \tag{26}$$

Although particles which are at rest in the coordinate system r, θ, ϕ will remain so, nevertheless it is evident from Eqs. (24) and (25), that the proper distance between such particles as measured with rigid meter sticks will in general be changing with the time, since the exponent g is itself a function of

[12] See reference 11, Eq. (4).

the time. Thus for the proper distance between a particle located at the origin $r=0$ and a particle permanently located at the coordinate distance $r=r$, we shall have

$$l_0 = \int_0^r \frac{e^{g/2}dr}{\sqrt{1 - r^2/R^2}} = e^{g/2}R \sin^{-1}\frac{r}{R} \tag{27}$$

and this will be increasing or decreasing with the time in accordance with the dependence of g on the time. Also in accordance with Eq. (26), the proper volume associated with a given coordinate range will be a function of the time, and for the proper volume of the universe as a whole we shall have

$$V_0 = \int_0^{2\pi}\int_0^{\pi}\int_0^{R} \frac{r^2 \sin\theta\, e^{3g/2}}{\sqrt{1 - r^2/R^2}} dr d\theta d\phi = \pi^2 R^3 e^{3g/2}. \tag{28}$$

In accordance with this result it is natural to consider $Re^{g/2}$ as the radius of the universe and to speak of an expanding universe if g is increasing with the time and of a contracting universe if g is decreasing with the time.

The change with time in the proper distance between objects in the universe leads to a shift in the observed wave-length of light coming from distant objects, a shift towards the red in an expanding universe and a shift towards the violet in a contracting universe. The magnitude of this shift is given by the formula[13]

$$\frac{\lambda_0 + \delta\lambda}{\lambda_0} = e^{(g-g_0)/2} \tag{29}$$

where g_0 is the value of the exponent occurring in the general expression for the line element at the time when the light was emitted with the original wave-length λ_0, and g is its value at the time the light is received and observed to have the wave-length $\lambda_0+\delta\lambda$.

In accordance with this formula we may regard the wave-length, which would be found by a local observer for any given quantum of light, as a quantity which is changing with the time in accordance with the change of g with the time. And, indeed, differentiating Eq. (29) with respect to the time we can evidently write

$$\frac{1}{\lambda}\frac{d\lambda}{dt} = \frac{1}{\lambda_0 + \delta\lambda}\frac{d}{dt}(\lambda_0 + \delta\lambda) = \frac{1}{2}\frac{dg}{dt} \tag{30}$$

as an expression for the fractional change in the wave-length of any given quantum with the time. Or in terms of frequency we can write

$$\frac{1}{\nu}\frac{d\nu}{dt} = -\frac{1}{2}\frac{dg}{dt} \tag{31}$$

as an expression for the change in the frequency of radiation with the time, ν being, of course, the frequency as measured by proper observers who are at rest with respect to the fluid in the universe and hence also at rest with respect to the coordinates r, θ, ϕ.

[13] See reference 11, Eq. (21).

This completes the statement of general properties of the non-static universe which we shall need in discussing our special model.

§11. Properties of non-static universe filled with black-body radiation.

We may now turn to the discussion of the special model in which we take the thermodynamic fluid filling the universe to be a uniform distribution of black-body radiation of the same proper density throughout, a proper observer being one who finds no net flow of radiation.

Under these circumstances we can obtain a great simplification in treatment since it is evident that the proper macroscopic density of the fluid ρ_{00} and its proper pressure p_0 will be related by the well-known expression connecting the density and pressure of radiation

$$\rho_{00} = 3p_0. \tag{32}$$

And this permits us to obtain an immediate relation between the pressure of radiation in such a universe and the time variable g, since by substituting in the general Eq. (23) we have

$$3\frac{d}{dt}(p_0 e^{3g/2}) + p_0 \frac{d}{dt} e^{3g/2} = 0 \tag{33}$$

and this can at once be integrated to give

$$p_0 = Ae^{-2g} \quad \text{and} \quad \rho_{00} = 3Ae^{-2g} \tag{34}$$

where A is the constant of integration, the pressure and density of radiation thus being quantities which decrease as the radius of the universe $Re^{g/2}$ increases.

As an important consequence of this result it now becomes possible to obtain a solution for g as a function of t. Substituting the expression for proper density given by Eq. (34) into Eq. (21) we obtain after some rearrangement

$$\frac{d}{dt}(e^g) = \pm \sqrt{32\pi A - \frac{4}{R^2}e^g + \frac{4}{3}\Lambda e^{2g}} \tag{35}$$

as a differential equation for the dependence of g on t, where the plus sign corresponds to an expanding universe and the negative sign to a contracting universe. Eq. (35) can itself then easily be integrated to give an explicit solution for g as a function of t. The form of the solution will depend on the sign of the cosmological constant Λ, and it is merely of interest for our present purposes to remark that for the case of a universe containing nothing but radiation there appears to be no solution, having physical reality, which would make g a periodic function of t.

As the most important consequence, however, of the expression for density given by Eq. (34), we can now show that the changes taking place in such a universe on account of the changing value of g are thermodynamically reversible. In accordance with Eq. (34) and the well known relation of Boltz-

mann connecting the density of black-body radiation with its temperature, we can write

$$\rho_{00} = 3Ae^{-2g} = aT_0^4 \tag{36}$$

where a is the Stefan-Boltzmann constant and T_0 is the proper temperature. Solving this for the temperature and substituting in the known expression for the entropy density of black-body radiation, we obtain

$$\phi_0 = \frac{4}{3} aT_0^3 = 4\left(\frac{a}{3}\right)^{1/4} A^{3/4} e^{-3g/2} \tag{37}$$

as an expression for the proper entropy density of our fluid.[14] On the other hand in accordance with Eq. (26) we have

$$dV_0 = \frac{r^2 \sin\theta\, e^{3g/2}}{\sqrt{1 - n^2/R^2}}\, dr d\theta d\phi \tag{38}$$

as an expression for the proper volume associated with the coordinate range $drd\theta d\phi$. Hence combining the two expressions (37) and (38), we can evidently write

$$\frac{\partial}{dt}(\phi_0 dV_0) = 0 \tag{39}$$

since g is the only quantity involved which depends on the time and this is seen to cancel out from the product.

The final result, however, is the very expression which we obtained in Part II (§7, Eq. (18)) as a general condition for a reversible process in relativistic thermodynamics. And since g and hence ϕ_0 will in general be changing in such a universe at a finite rate, we have thus actually illustrated by a specific example the possibility provided by relativistic thermodynamics for reversible processes to take place at a finite rate.

§12. Interpretation by an ordinary observer of phenomena in an expanding universe filled with radiation.

Turning our attention now in particular to the case of expansion, with the radius $Re^{g/2}$ increasing with the time, we can show that the special model of a universe, filled with black-body radiation and expanding reversibly without increase in entropy, would nevertheless exhibit important phenomena which

[14] The relations connecting energy density and entropy density with temperature, used in (36) and (37), presuppose that the frequency distribution of the radiation remains that for black-body radiation for all values of g. This introduces no difficulty, however, since even if there were a tendency for the frequency distribution to change away from that for black-body radiation, as the size of the universe changes, this could be prevented by the introduction of a small amount of material to act as a catalyst; and in actuality there is of course no such tendency since it would involve a decrease in entropy. In addition it can be shown in detail that the dependencies of frequency and energy density on g given by Eqs. (31) and (34) are such as to preserve the black-body distribution of frequency for all values of g, if we have such a distribution for one value of g.

would be interpreted by an ordinary observer as similar to phenomena in the actual universe which have been regarded in the past as important evidence for an increasing entropy of the universe. To obtain a description of these phenomena, we shall consider that the observer in question marks out a small region of the universe in his immediate vicinity, using rigid meter sticks, and then studies the changes taking place in this region. We shall then show that the observer will find the density of energy in this region and the total energy content of the region continually decreasing with the time, its temperature dropping, the number of light quanta leaving the region always greater than the number entering, and the average frequency of the quanta which leave greater than the average frequency of those that enter. Evidently our ordinary unsophisticated observer would interpret these findings as evidence that his immediate neighborhood was cooling off by radiation into the colder depths of space, and with a knowledge only of the classical thermodynamics he would conclude that the entropy of the universe was increasing at an enormous rate, in spite of the fact that the relativistic thermodynamics, which must be used under the circumstances, actually shows that there would be no increase in entropy in such a universe. The analogy between the phenomena interpreted by this unsophisticated observer as leading to an increase of entropy and phenomena in the actual universe which have hitherto been interpreted in a similar manner is close enough so that we must certainly be cautious lest we draw too hasty conclusions as to increases in entropy in our actual universe.

To proceed now to the detailed exposition, let us consider that the observer in our idealized model of the universe is located for convenience at the origin of the r, θ, ϕ system of coordinates and is provided with a rigid scale of proper length dl_0. With the help of this scale he marks out a small sphere around the origin of constant proper radius l_0, which gives him a small region of the universe in his immediate vicinity to serve as the subject of his studies.

For the relation between the constant proper radius of this sphere and the coordinate r of its boundary we may evidently write in accordance with Eq. (24)

$$l_0 = \int_0^r \frac{e^{g/2}dr}{\sqrt{1 - r^2/R^2}} = e^{g/2}R \sin^{-1}\frac{r}{R} \tag{40}$$

and for the case in hand where the sphere considered is very small compared with the whole universe, so that r is small compared with R, we obtain from this the approximate relation

$$r \approx l_0\, e^{-g/2}. \tag{41}$$

Since the proper radius of the sphere l_0 is constant by hypothesis, we note that the coordinate r of its boundary is a quantity which is decreasing with the time in an expanding universe owing to the increase in g with time.

For the proper volume of this sphere contained within the radius l_0 we can evidently write in accordance with Eq. (26)

$$V_0 = \int_0^r \frac{4\pi r^2 e^{3g/2} dr}{\sqrt{1 - r^2/R^2}} = 4\pi e^{3g/2} R \left| -\frac{r}{2}\sqrt{R^2 - r^2} + \frac{R^2}{2} \sin^{-1}\frac{r}{R} \right|_0^r . \tag{42}$$

Developing this in the form of a series in r/R and neglecting higher powers, we obtain

$$V_0 = 4\pi e^{3g/2} R^3 \left(-\frac{1}{2}\frac{r}{R} + \frac{1}{4}\frac{r^3}{R^3} + \frac{1}{16}\frac{r^5}{R^5} + \cdots + \frac{1}{2}\frac{r}{R} + \frac{1}{12}\frac{r^3}{R^3} + \frac{3}{80}\frac{r^5}{R^5} + \cdots \right) \approx \frac{4}{3}\pi r^3 e^{3g/2}. \tag{43}$$

And substituting the value of r given by Eq. (41), we obtain for the proper volume of the sphere in terms of its proper radius l_0, as a close approximation, the result which might be expected

$$V_0 = \frac{4}{3}\pi l_0^3 \tag{44}$$

which is a constant independent of the time.

We may now consider the nature of the observations which our observer would find in studying this sphere of constant measured radius which he has marked off.

As a result of Eq. (34), the proper energy density at every point in our special model of the universe would be changing with the time t in accordance with the expression

$$\frac{1}{\rho_{00}}\frac{d\rho_{00}}{dt} = -2\frac{dg}{dt}. \tag{45}$$

Moreover, the measurements of energy density which our observer would make in his immediate neighborhood would actually be measurements of proper energy density, and from the form of the line element (19) the proper time which he uses would agree with the coordinate time t. Hence it is evident that our observer would find the energy density in his vicinity to be decreasing with the time in accordance with Eq. (45).

Furthermore, in accordance with Eq. (44), the proper volume of his sphere of constant measured radius is itself independent of the time. Hence it is evident that our observer would find the total energy content E_0 of his sphere decreasing at the rate

$$\frac{1}{E_0}\frac{dE_0}{dt} = -2\frac{dg}{dt}. \tag{46}$$

In addition, owing to the relation between energy density and temperature for black-body radiation given by Eq. (36), it is evident that our observer would find the temperature in his vicinity to be dropping at the rate

$$\frac{1}{T_0}\frac{dT_0}{dt} = -\frac{1}{2}\frac{dg}{dt}. \tag{47}$$

Still further, since the total number of light quanta in the universe would be independent of the time, and the proper volume of the universe as a whole would be increasing with the time while the proper volume of the observer's sphere remained constant, it is evident that the observer would find a larger number of light quanta leaving his sphere per second than entering. To calculate this excess we may evidently write for the number of quanta n inside the sphere in terms of the total number of quanta N in the universe

$$n = \frac{\frac{4}{3}\pi l_0^3}{\pi^2 R^3 e^{3g/2}} N \tag{48}$$

where the numerator of the fraction is the proper volume of the sphere as given by Eq. (44) and the denominator is the total proper volume of the universe as given by Eq. (28). And carrying out a logarithmic differentiation of this with respect to the time we obtain

$$\frac{1}{n}\frac{dn}{dt} = -\frac{3}{2}\frac{dg}{dt} \tag{49}$$

which gives the net loss per unit time in the number of quanta within the observer's sphere. The result so obtained, when combined with the rate at which the frequencies of the quanta are decreasing with the time as given by Eq. (31), is just sufficient to account for the rate of decrease in the proper energy of the observer's sphere as given by Eq. (46).

Finally, we may point out a curious circumstance which would reinforce our unsophisticated observer in his interpretation of the above phenomena as radiation into surroundings of lower temperature. Let us suppose that our observer, ever active in his scientific investigations, stations one of his assistants on the boundary of his sphere at the fixed distance l_0 from the origin as measured with rigid meter sticks, and instructs him to observe the average frequency of the light entering and leaving the sphere through its surface. This assistant will not be at rest in the coordinate system r, θ, ϕ, but in accordance with Eq. (41) will have the coordinate velocity

$$\frac{dr}{dt} = -\frac{1}{2} l_0 e^{-g/2}\frac{dg}{dt} = -\frac{1}{2} r \frac{dg}{dt}. \tag{50}$$

Hence, since it is evident that the average frequency of the radiation would be independent of direction for an observer at rest in the coordinate system, this assistant will find the average frequency of the radiation entering the sphere less than that of the radiation leaving the sphere, as a result of the Doppler effect corresponding to the velocity given by Eq. (50).

This completes a considerable chain of evidence which would lead an ordinary observer, unfamiliar with the expansion of the universe, to conclude that the region in his immediate neighborhood was cooling off by radiation into surroundings of lower temperature, in spite of the fact that the changes taking place in the model actually involve no increase in entropy. The analogy

between the findings of this observer in the hypothetical model and those of the classical thermodynamist in the actual universe is very striking.

PART IV. CONCLUSION

§13. Summary.

In the foregoing article an attempt has been made to show the bearing of relativistic thermodynamics on the well-known problem of the entropy of the universe as a whole. The origin of this problem lies in the difficulties encountered by the classical thermodynamics,—first in failing to account for the presumed fact that the entropy of the universe has always been increasing at an enormous rate and nevertheless has not yet reached its maximum value,—and second in failing to allow an emotionally satisfactory feeling towards our universe whose ultimate fate would be the stagnation of "heat-death."

In the present article a brief description was first given of various older contributions to the solution of this problem, which have been based on the standpoints of the classical thermodynamics and statistical mechanics. This was done in order to show the very different character of the new contribution proposed in this article. A summarized account of the nature of this contribution may now be given.

The problem of the entropy of the universe arises because of the commonly accepted conclusion that the entropy of the universe is actually increasing at an enormous rate, and this conclusion is in turn based on the presumption, familiar in classical thermodynamics, that thermodynamic processes cannot be taking place at a finite rate, as observed, and at the same time reversibly without increase in entropy. The general nature of the contribution to the problem offered by relativistic thermodynamics lies in showing that there can be thermodynamic processes which take place both reversibly and at a finite rate.

To illustrate this difference between the classical and relativistic thermodynamics, we may consider the possibility of carrying out a reversible change in the thermodynamic properties of a finite portion of thermodynamic fluid. In the classical mechanics it is found that no internal motions of the fluid, no flow of heat, and no change in volume can be allowed to take place at a finite rate and hence that no change at all in the thermodynamic properties of the fluid can take place at a finite rate, the entropy density of the fluid remaining constant in accordance with the equation

$$\frac{d\phi_0}{dt} = 0.$$

On the other hand, in relativistic thermodynamics it appears possible to allow changes in the proper volume of the fluid, due to changes in the gravitational potentials, to take place at a finite rate and still maintain reversibility. Indeed, the condition for reversibility is found to be satisfied if we have at each point in the fluid the relation

$$\frac{\partial}{\partial x_4}\left(\phi_0\sqrt{-g}\,\frac{dx_4}{ds}\,dx_1dx_2dx_3\right) = \frac{\partial}{\partial x_4}(\phi_0 dV_0) = 0$$

and this permits a finite rate of change in the proper entropy density ϕ_0 with the time x_4, provided it satisfies the equation

$$\left(\sqrt{-g}\,\frac{dx_4}{ds}\right)\frac{\partial\phi_0}{\partial x_4} + \phi_0\frac{\partial}{\partial x_4}\left(\sqrt{-g}\,\frac{dx_4}{ds}\right) = 0.$$

To exhibit the nature of the reversible changes at a finite rate thus permitted in relativistic thermodynamics, we may consider the highly idealized model of a non-static universe filled with black-body radiation as our thermodynamic fluid. It is found that the radius and total proper volume of such a universe could be changing at a finite rate with the time and yet reversibly without increase in entropy.

Furthermore, if we take the case of an expanding universe and consider an observer who marks out with rigid meter sticks a small region of the universe in his vicinity, it can be shown that he would find the energy density, the energy content, and the temperature of this region decreasing with the time, and in addition would find the number of light quanta leaving the region per second greater than the number returning and the average frequency of those passing outward through the boundary greater than that of those returning. He would thus be led to interpret the phenomena taking place in such a universe as a flow of radiation from his immediate neighborhood out into the colder regions of space, in spite of the fact that the changes in the universe would in reality be taking place without any increase in entropy.

The general nature of the contribution to the problem of entropy made in this article has thus been to show that phenomena which have hitherto been regarded from the point of view of classical thermodynamics as furnishing unmistakable evidence for an increasing entropy in the universe are not necessarily leading to any increase in entropy at all, and to emphasize the necessity for analyzing the phenomena of the universe from the more acceptable point of view of relativistic thermodynamics before conclusions are drawn as to what extent the entropy of the universe is increasing if at all.

§14. Critique.

Finally a few words of criticism will not be out of place. The foregoing statement as to the nature of the contribution made in this article carries with it at least the possible implication that an analysis of the phenomena of the actual universe from the standpoint of relativistic thermodynamics would show that there are in reality no important changes at all taking place in the entropy of the universe.

I feel, however, that although the article has clearly demonstrated the necessity of using relativistic thermodynamics in analyzing the entropy changes of the universe as a whole, it would be premature to assert too precisely what is to be expected as the result of such an analysis until it has been applied to a model of the universe which is not so over-simplified as the one

employed in this article. This model of a universe, containing nothing but radiation, neglects two of the most characteristic features of the actual universe, namely the presence of matter and its high degree of concentration into stellar systems. At a later time I hope to give more consideration to these properties of the universe. They appear, however, greatly to increase the mathematical complexity of the problem and for this reason I have contented myself for the present with a very simple model, which can nevertheless give us considerable insight into the problem of the entropy of the universe.

One feature of the model which was mentioned in §11 should perhaps be emphasized, namely that there appear to be no periodic solutions of Eq. (35) for g as a function of t which would have physical interest. Hence if we had an expanding model of the kind considered it would continue to expand, reversibly to be sure, but without actual return to its original condition. Our model is so over-simplified, however, that we must no conclude therefrom that periodic solutions would not be of interest for the actual universe.

Further it should perhaps also be emphasized again that the theory of fluctuations may play an important part in a relatively complete treatment of the entropy of the universe. At the present time, however, we cannot say just how large this part may be.

In conclusion then, it has apparently been definitely demonstrated that the problem of the entropy of the universe as a whole must be treated with the help of relativistic rather than classical thermodynamics, and it has been shown that the application of relativistic thermodynamics to a highly oversimplified model of the universe gives results of great interest. It remains for the future, however, to consider the application of relativistic thermodynamics to more complicated models which would give a better approximation to the actual universe.

ON THE RESOLVING POWER OF A PRISM SPECTROMETER FOR THE INFRARED

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Abstract

The resolving power of a spectrometer in the infrared is limited by the rate at which energy passes through the exit slit of the spectrometer. Calculation of the energy available for activating a thermocouple, under condition that the exit slit embrace the same frequency range $\Delta\nu$ of spectrum at all times, gives information on the attainable resolving power at various wave-lengths and with various prisms. The best dispersing angle for a sylvine prism to be used from 8 to 22μ is from 70° to 75°. A lamellar prism construction is described.

Introduction

In the spectral region where a photographic plate, which measures the energy received during the time of exposure, is used, the resolving power of a spectrometer is limited by interference effects. However, in the infrared where a thermocouple or radiometer is used one does not measure the energy received over an arbitrary period of time but the rate at which energy is received. This available energy rather than interference effects places the limit on the resolving power of the spectrometer.

It was the purpose of this investigation to make calculations of the energy available for activating a receiver (such as a thermocouple). The energy of a continuous spectrum passing through the exit slit, with both slits equal, is proportional to the square of the slit width, so that if the value for the available energy at any particular wave-length and for a particular dispersing prism is greater, by a factor α, than the energy necessary to give a definite response of the receiving device, then the spectrometer slits may be closed by a factor $1/\alpha^{1/2}$ and still give a practical deflection. The available energy is therefore a measure of the resolving power which is attainable under varying conditions as long as the limit set by interference effects is not exceeded.

The calculation of available energy is instructive on account of the information that it gives regarding the resolving power attainable in various regions of the spectrum. The determination of the absorption spectrum of a gas in the infrared consists of a study of the heat radiations emitted from some convenient source and the changes in spectral energy distribution which result from the introduction of the gas into the radiation path. The spectrum emitted from a heated body possesses very little energy at long wave-lengths since the emission cannot exceed that from a black body which varies inversely with the fourth power of the wave-length. This scarcity of available

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energy at long wave-lengths would seem to place a serious limitation upon the character of experimental work that might be done at long wave-lengths. However, the results of Robertson and Fox[1] with a rocksalt prism on the oscillation-rotation spectrum of ammonia and similar molecules shows a definite improvement in resolution at the longer wave-lengths. These calculations will show in a quantitative way that similar improvement at long wave-lengths is to be expected for a sylvine prism.

The calculation of available energy for various prisms shows the best prism to use for a particular spectral region. For the entire spectral range for which sylvine is a useful prism material, it is best to have as the dispersing angle of the prism 70 to 75 degrees. Usually a 60° prism is considered best but this is neither obvious nor a consequence of the classical works of Pickering[2] and of Wadsworth.[3] These authors made calculations of the best dimensions for prisms made from materials having values for the refractive index varying between 1.5 and 1.8. Their calculations do not hold because sylvine has refractive indices below 1.5 in the infrared, also the formula used by Pickering and Wadsworth for the transmission of a prism is invalid except when the absorption is very low.

Priliminary Considerations

When a band system in the infrared is plotted with wave number rather than wave-length as the abscissa one gets a more natural picture, since the fineness of structure is then approximately the same throughout the spectrum. On the other hand, if wave-length is used as abscissa, the structure appears coarser at longer wave-lengths and in fact if $\Delta\nu$ is taken as a measure of the fine structure of the band system the corresponding $\Delta\lambda$ becomes greater at longer wave-lengths according to the formula

$$\Delta\lambda = \frac{\lambda^2\Delta\nu}{c}.$$

This means that if the slit of the spectrometer is adjusted so that the wave-length interval in the slit is increased proportionally with λ^2 it will embrace the same frequency range of spectrum. The energy passing through the exit slit is proportional to the spectral energy density of illumination of the slit, E_λ, multiplied by the square of the slit width. For a black body at long wave-lengths E_λ is proportional to λ^{-4} while for an ideal spectrometer having constant dispersion and constant efficiency the slit width, s, would be proportional to λ^2 and $E_\lambda s^2$, the energy passing through the exit slit, would be independent of λ. By constant efficiency it is meant that the same fraction of the energy of various wave-lengths is lost by reflection at the various surfaces in the optical path and by absorption in the prism. This means that the resolving power measured by the rational magnitude $\Delta\nu$ will be the same throughout the spectrum.

[1] R. Robertson and J. J. Fox, Proc. Roy. Soc. **A120,** 128 (1928).
[2] Pickering, Phil. Mag (4), **36,** 39 (1868).
[3] F. L. O. Wadsworth, Astrophys. J. **2,** 264 (1895)

For a spectrometer which is not ideal the energy passing through the exit slit increases as the dispersion increases and decreases as the efficiency decreases. $\delta n/\delta\lambda$ for the materials transparent in the infrared increases at longer wave-lengths while the transparency decreases. The dispersion factor predominates at first and so the available energy (when the slit width is constant as measured by $\Delta\nu$) increases and greater resolving power is attainable at longer wave-lengths. This for sylvine is a result similar to the experimental results of Robertson and Fox. The available energy passes through a maximum and rapidly decreases as the transparency factor becomes predominate. When the dispersing angle of the prism increases the dispersion increases, at first slowly, then rapidly, while the light lost by reflection increases. It was for the purpose of arriving at the best compromise between these varying factors that the following calculations were made.

Energy Available to Activate Receiver

For a simple prism spectrometer the energy, e, passing through the exit slit is given by the following expression

$$e = E_\lambda s_1 l_1 \frac{A}{f_1^2} \frac{s_2}{f_2 \dfrac{d\theta}{d\lambda}} TFR.$$

The symbols are defined by the following formulas:

E_λ is the spectral energy density of illumination of the entrance slit and for long wave-lengths this is given by the Rayleigh-Jeans formula.

$$E_\lambda = \frac{4\pi kt}{\lambda^4}.$$

s_1 and l_1, are width and length respectively of the entrance slit.

A is the effective area of the collimating mirror of the spectrometer. For a large collimating mirror this is the area of the prism face ($h \times b$ if h is the heighth of prism face and b the length) projected on the plane of the mirror face. If i is the angle of incidence of the light on the prism face, A is defined by the equation $A = h \times b \cos i$.

f_1 and f_2 are the focal lengths respectively of the collimating and telescope mirrors.

s_2 is the width of the exit slit.

$d\theta/d\lambda$ is the dispersion of the prism and it may be broken up into two factors $(\partial\theta/\delta n) \times \partial n/\partial\lambda$. For a prism at minimum deviation $\partial\theta/\partial n$ is given by $2 \sin(\phi/2)/\cos i$ where ϕ is the dispersing angle of the prism. Values of $\partial n/\partial\lambda$ are defined by the empirical formula given by Rubens[4] for the index of refraction of sylvine.

T is the transmission of the prism. This is given by the formula

$$T = \frac{1}{\kappa\tau}(1 - e^{-\kappa\tau})$$

[4] Rubens, Ann. d. Physik **54**, 476 (1895); **60**, 724 (1897).

The absorption coefficient is represented by κ and the width of the prism opposite the dispersing angle is represented by τ. For values of $\kappa\tau$ less than 0.1 the values of T are given approximately by the formula used by Pickering and Wadsworth in their work, $T=e^{-\kappa\tau/2}$. For values of $\kappa\tau$ greater than 5 the values of T are given approximately by $1/\kappa\tau$. Table I gives values of T for various values of $\kappa\tau$.

TABLE I.

$\kappa\tau$	T	$\kappa\tau$	T	$\kappa\tau$	T	$\kappa\tau$	T
0.01	0.995	0.11	0.946	0.1	0.952	1	0.632
.02	.989	.12	.943	.2	.906	2	.432
.03	.985	.13	.938	.3	.864	3	.317
.04	.980	.14	.934	.4	.824	4	.245
.05	.975	.15	.929	.5	.787	5	.198
.06	.970	.16	.924	.6	.752	6	.166
.07	.966	.17	.919	.7	.719	7	.143
.08	.961	.18	.915	.8	.688	8	.125
.09	.956	.19	.911	.9	.659	9	.111
.10	.952	.20	.906	1.0	.632	10	.100

F is a factor which takes account of the loss of light due to reflections at the two prism surfaces and is represented by the following formula,

$$F = \left\{ \frac{1}{2}\left[1 - \frac{\sin^2(i-r)}{\sin^2(i+r)}\right] + \frac{1}{2}\left[1 - \frac{\tan^2(i-r)}{\tan^2(i+r)}\right] \right\}^2$$

where r is the angle of refraction at the prism face.

R is the total reflectivity of all the spectrometer mirrors and is considered constant. For eight normal reflections from polished silver the loss of light is 8 percent at 10μ and 4 percent at 20μ.

If $f_1=f_2$ and if the spectrometer slits are equal and always adjusted so that the frequency interval they subtend is constant then s_1 and s_2 may be substituted for by the expression

$$s_2 = s_1 = f_1 \frac{d\theta}{d\lambda} \frac{\lambda^2 \Delta\nu_0}{c}$$

where $\Delta\nu_0$ corresponds to the constant frequency interval embraced by the slits.

Substituting in the formula for e gives

$$e = \frac{8\pi k l \Delta\nu_0^2 hbR}{c^2 f_1} TF \frac{\partial n}{\partial\lambda} \sin\frac{\phi}{2}$$

or

$$e \propto \epsilon = TF \frac{\partial n}{\partial\lambda} \sin\frac{\phi}{2}.$$

Values of F for various prism angles, ϕ, and various wave-lengths are given in Table II. For the calculation of ϵ given in Table III, τ was given the value 10 centimeters.

TABLE II. *Values of F for various ϕ and λ.*

ϕ	10.02μ	14.14μ	17.68μ	20.6μ	22.5μ
0°	0.931	0.936	0.942	0.947	0.971
60°	.910	.917	.925	.934	.966
70°	.873	.885	.898	.901	.957
75°	.799	.847	.846	.886	.950
80°	.727	.768	.805	.840	.937
85°	.419	.563	.662	.735	.915
90°	—	—	—	.244	.877

TABLE III. *Values of ϵ for various ϕ and λ.*

ϕ	8.84μ	10.02μ	11.79μ	12.96μ	14.14μ	15.91μ	17.68μ	20.6μ	22.5μ
15°	4.0	4.1	4.3	5.4	6.8	7.4	7.9	6.5	5.1
30°	7.9	9.1	10.8	11.9	12.9	13.5	13.5	8.1	5.4
45°	11.6	13.0	15.8	17.2	18.8	18.4	17.7	8.2	5.6
60°	15.0	17.2	20.3	21.7	23.0	22.1	19.6	8.2	5.6
70°	16.5	18.9	22.4	23.6	24.8	23.6	19.9	8.1	5.5
75°	16.0	18.4	22.2	23.5	25.0	23.5	19.6	8.0	5.4
80°	14.0	17.7	21.2	22.5	23.6	22.7	18.5	7.5	5.4
85°	8.2	10.7	14.6	16.5	18.1	18.9	15.5	5.4	5.2

It would seem impractical to narrow the slits narrower than the frequency interval $\Delta\nu'$ corresponding to the theoretical resolving power of the spectrometer. For a prism spectrometer this is given by the Rayleigh formula.

$$\Delta\nu' = \frac{-c}{\lambda(\partial n/\partial\lambda)\tau}.$$

If the absorption coefficient is high only the apex of the prism will transmit radiation and the value of τ to be substituted in the formula is much less than the actual value of τ. In order to get an idea of how this limiting frequency interval, $\Delta\nu'$, varies as one goes deeper into the infrared it may be calculated using a value corresponding, for that wave-length in question, to a prism having a transmission of 95 percent. The values of $\tau_{T=.95}$ are given in Table IV

TABLE IV. *Values of $\tau_{T=.95}$ and $\Delta\nu'$ for various wave-lengths.*

λ	11.79μ	12.96μ	14.14μ	15.91μ	17.68μ	20.6μ	22.5μ
κ	0.004	0.0175	0.0270	0.065	0.135	0.515	1.00 cm^{-1}
$\tau_{T=.95}$	25	5.72	3.71	1.54	.74	.19	.10 cm
$\Delta\nu'$	.75	2.6	3.4	6.2	9.9	26.4	38.4 cm^{-1}

together with corresponding values of $\Delta\nu'$. It is interesting to compare these limiting frequencies with the resolving power successively realized by Burmeister, Eva von Bahr, Brinsmade and Kemble, Imes and Randall, and Meyer and Bronk in their classical investigations of the fundamental oscillation band of HCl. Their slit widths reduced to the same units used in Table IV are respectively 40, 10, 7, 4 and 3 cm^{-1}.

When only the apex of the prism transmits appreciably and it is not possible to realize the limiting resolving power on account of the insensitivity of

the receiver one may double or quadruple the energy passing through the exit slit by using two or four identical prisms side by side which are tall compared with τ. Such an arrangement is shown in Fig. 1. Since it is much easier to make a plane parallel plate than to make a prism whose faces make a prescribed angle with each other, an alternative arrangement is illustrated by Fig. 2. The back of each parallel plate is silvered by evaporation, the plates

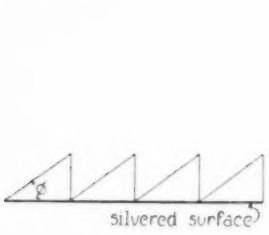

Fig. 1.

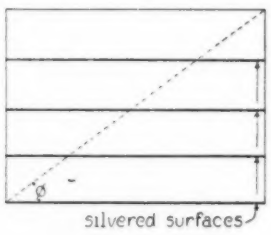

Fig. 2.

are waxed together and the ensemble cut and polished along the dotted line so as to give a lamellar prism with dispersing angle 35° to 37.5°. This will form a Littrow half prism into which the light will not need to penetrate deeper than the thickness of the parallel plates used. It is, however, more advisable to use a prism which is more transparent in the desired spectral region.

Conclusion

From the values of ϵ given in Table III and the values of $\tau_{T=.95}$ and $\Delta\nu'$ given in Table IV, we may draw the following conclusions.

1. A dispersing angle of 70° to 75° is best for a sylvine prism to be used from 8 to 22μ. Table III shows the available energy for these prism angles to be greater for all wave-lengths out to 18μ. Beyond 18μ, there is so little difference in the available energy that the construction of a special 15° prism for this region is not justified.

2. A sylvine prism with a 10 cm base is useful to 18μ. In spite of the fact that the energy for illuminating the entrance slit of the spectrometer decreases with the fourth power of the wave-length, it will be observed from Table III that the energy available for activating a thermocouple increases. This means that the resolving power increases at longer wave-lengths as long as the available energy, rather than interference effects, places the limit on the resolving power of the spectrometer.

3. Values of $\tau_{T=.95}$ in Table IV show that only the apex of the prism transmits radiations. The available energy may be increased several fold by the use of a lamellar prism construction. This should make it possible to realize approximately the theoretical resolving power of one of the lamella. Such a lamellar prism would be particularly useful when the radiations are to be further dispersed with a grating. It is possible that the use of another prism material, such as potassium iodide (transparent to wave-lengths greater than 33μ) would be better. However, since no material is yet known which is more transparent than potassium iodide it may be advisable to use a lamellar

prism of this material in order to extend the region open to prism spectroscopy as far as possible. The optical properties of potassium bromide and potassium iodide are being investigated by the author so that a set of values of ϵ for all the infrared prism materials may be compiled.

4. An examination of the proportionality factor between e and ϵ shows the available energy is inversely proportional to the focal length of the spectrometer collimator. This result indicates that a spectrometer of the Pfund type would give the best resolution.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Effect of Meteors on Radio Transmission Through the Kennelly-Heaviside Layer

A consideration of the available data on meteor trains indicates (1) that meteors expend the larger part of their energy in the Kennelly-Heaviside layer,[1] that is, in that region of the upper atmosphere which controls the propagation of all long distance radio waves; (2) that a large fraction of the energy of a meteor goes into ionization of the air around its path;[2,3] (3) that this ionization extends to a considerable distance from the actual path[4]—in some cases, several kilometers or more—and (4) that it lasts for some minutes after the meteor has passed.[4]

It is interesting to calculate the order of magnitude of the ionic concentration which may be produced and to compare it with the concentration which is generally assumed in order to explain short wave radio phenomena. Meteors are believed to vary in mass from a few milligrams to several kilograms and larger, according to different estimators. If the mass of a meteor is taken as one gram, its velocity as 40 km/sec., its length of path as 200 km and the range of ionization around the path as 1/2 km, the concentration of ionization on the above assumptions would be of the order of 10^6 ions per cc. The maximum ionization deduced from radio data is of the order of 10^5 electrons per cc. It is therefore apparent that transmission of radio signals might be markedly affected by the presence of meteors along the path.

Data taken during radio measurements of the heights of the ionized layer, furnish evidence for such an effect. Thus Heising[5] finds that the deflecting layer seems to experience very sudden drops as though a large amount of ionization suddenly appeared, accompanied for a moment by turbulence, after which the layer gradually returns to the normal height. The frequency of such sudden variations is reasonably consistent with the number which would be expected for the particular length of path used, on the assumption of 10^9 meteors of random direction per day for the whole earth.[6]

The orbital motion of the earth increases the relative velocity of the meteors which are observed after midnight and it is an observed fact that the number of meteors has a maximum between 2:00 and 3:00 A.M. Both of these facts would increase the contribution of ionization which is due to meteors and might even result in a lowering of the Kennelly-Heaviside layer after midnight. A number of investigators have observed such a drop after midnight. Moreover, on the basis of the above calculations and assuming that the ions produced have an average life of one hour, the total ionization produced by meteors is of the correct order of magnitude to produce the effect observed.

The foregoing evidence, while admittedly sketchy, indicates that the ionizing effect of meteors in the Kennelly-Heaviside regions may be an important factor in short wave radio propagation through the upper atmosphere. It is planned to make tests during future meteoric showers in order to obtain further information on the subject.

A. M. SKELLETT
Bell Telephone Laboratories, Inc.,
New York, New York,
April 7, 1931.

[1] Humphrey, Physics of the Air, p. 23.
[2] Lindeman and Dobson, Proc. Roy. Soc. of London, **A411,** 102 (1923).
[3] Maris, Terrest. Mag. and Atmos. Elect. **34,** 309 (1929).
[4] Olivier, Meteors, p. 147.
[5] Heising, Proc. I.R.E. **16,** 75, (1928).
[6] Shapley, Harv. Circ. No. 317, May, 1928.

Raman Spectrum of the Hydroxyl Ion with High Dispersion

The Raman spectrum of a 10*N* aqueous solution of potassium hydroxide was photographed with a Hilger El large quartz spectrograph, using for excitation a hot-cathode helium arc of length 45 cm. The Pyrex tube which contained the solution was surrounded by a filter tube of nickel oxide glass, and the light was focused on it by an elliptical reflector. An exposure time of 100 hours was required.

The spectrum obtained consists of a single broad line having a fairly well defined intensity-maximum which corresponds to a frequency shift of 3603 ± 4 cm^{-1}. This is in good agreement with the value of 3615 ± 25 cm^{-1} recently reported by Woodward.[1] It is somewhat lower than the shift of 3630 cm^{-1} found by Krishnamurti[2] in crystalline sodium hydroxide. The line has a width of about 30 cm^{-1}. That it must be attributed to the hydroxyl ion is beyond doubt.

It was observed that the presence of dissolved sodium or potassium hydroxide greatly influences the structure and the intensity of the water band. We have studied this effect in solutions of various concentrations, using a spectrograph of smaller dispersion. The results will soon be reported in detail.

J. L. Thompson
J. Rud Nielsen
University of Oklahoma,
May 27, 1931.

[1] L. A. Woodward, Phys. Zeits. **32,** 261 (1931).

[2] P. Krishnamurti, Indian J. Physics **5,** 651 (1930).

The Relative Abundance of the Oxygen Isotopes, and the Basis of the Atomic Weight System

Mecke and Childs,[1] as the result of a detailed quantitative investigation of the *A* and *A'* bands of oxygen, find the relative abundance of the oxygen isotopes O^{16} and O^{18} to be 630:1, in sharp contrast to the value 1250:1 found by Babcock[2] and 1075:1 found by Naudé.[3] We have made a careful study of Mecke and Childs' paper, and find several rather doubtful theoretical assumptions. We have accordingly recalculated a portion of their data, using a method that appears to us to be more reliable. Their final result is, however, not essentially changed, and it therefore seems unnecessary to publish the details.

We have also examined Babcock's assumptions, and find two sources of possible error, one due to the fact that the rotational energy levels of the $O^{16}.O^{18}$ molecule differ from those of the $O^{16}.O^{16}$ molecule, and the other due to the fact that, in Babcock's work, the mean temperature of the $O^{16}.O^{18}$ molecule (in the atmosphere) differs from the temperature of the $O^{16} \cdot O^{16}$ molecule (in the laboratory). Both the energy and the temperature affect the Boltzmann factor, but fortunately the two errors thus introduced by Babcock's neglect of this factor tend to cancel. We find that for the lines used by Babcock,[4] the maximum resulting error is not more than about ten percent, and so is quite negligible.

Mecke and Childs suggest several possible sources of error in the work of Naudé, but we do not have the information necessary in order to discuss these suggestions. As far as the work of Babcock and of Mecke and Childs is concerned, it would appear that the discrepancy must be due mainly to experimental and not to theoretical errors. It would also appear that the Mecke and Childs result is entitled to much greater weight.

Assuming for the sake of argument that the abundance ratio is really 630 to 1, it follows, as noted by Mecke and Childs, that atomic masses based on $O^{16}=16$ should be 2.2 parts in 10^4 greater than those based on the chemical system $O=16$. It is accordingly of importance to test Aston's mass-spectrograph results[5] on this new basis. Aston,[6] Birge,[7] and Naudé[3] have previously considered this mat-

[1] R. Mecke and W. H. J. Childs, Zeits. f. Physik **68,** 362 (1931).

[2] H. D. Babcock, Proc. Nat. Acad. Sci. **15,** 471 (1929).

[3] S. M. Naudé, Phys. Rev. **36,** 333 (1930).

[4] According to a personal communication from Babcock, only the first few lines of the *P* branch were used.

[5] F. W. Aston, Proc. Roy. Soc. **A115,** 487 (1927).

[6] F. W. Aston, Nature **123,** 488 (1929).

ter, but the conclusions depend markedly on the values adopted for the chemical atomic weights. One of us[7] has already found that the rounded values ordinarily published in atomic-weight tables are not sufficiently accurate for a discussion like this.

Nearly all of Aston's precision measurements are concerned, unfortunately, with elements that are known to consist of a mixture of isotopes. In such cases it is necessary to know the relative abundance of the isotopes of the element in question, as well as of oxygen, in order to compare Aston's result with the chemical atomic weight. For elements like carbon and nitrogen, the two resulting corrections (for oxygen, and for the element in question) tend to cancel, so that Aston's result should agree closely with the chemical atomic weight. Thus in the case of carbon the most probable atomic weight[7] is 12.0025. Aston's mass C^{12} is 12.0036, which becomes 12.0010 on division by 1.00022 in order to reduce to the chemical scale. Then to obtain an atomic weight of 12.0025, the relative abundance C^{12}/C^{13} should be 650. King and Birge[8] give 400 for this figure, but their discussion shows that 650 is an equally possible value.

The best atomic weight of nitrogen[9] is 14.008. Aston finds $N^{14}=14.008$. To bring the two results into agreement requires a relative abundance $N^{14}/N^{15}=320$. Naudé found that the abundance $N^{14}/N^{15}=0.65$ of O^{16}/O^{18}. Using Mecke and Childs' value of O^{16}/O^{18}, one obtains $N^{14}/N^{15}=409$, a very satisfactory agreement.

The best atomic weight of helium appears to be[7] 4.0018. Aston obtained 4.00216, or 4.00127 on the chemical scale. The discrepancy is only 1.1 parts in 10^4, which is within the published limits of error. The most accurate atomic weight of fluorine is due to Moles and Batuecas[10], from the molecular weight of FCH_3. Using the present best values for C and H, their result is 18.995 ± 0.005. Aston obtains 19.000, or 18.996 when reduced to the chemical scale. The agreement is entirely satisfactory. In the case of iodine, Aston's result is identical with the best chemical value. The connection with oxygen, in the mass-spectrograph work, is rather indirect, and it is therefore doubtful if this result can be considered to furnish independent evidence on the question. In the case of phosphorus it is the chemical value that is uncertain.

Of the elements that permit an accurate comparison of the chemical and mass-spectrograph results, there remains only hydrogen. The chemical value[7] is 1.00777 ± 0.00002 (probable error), as compared with Aston's 1.00778 ± 0.00015 (*limit* of error). Aston's value, reduced to the chemical scale, is 1.00756 and the discrepancy appears to be outside the limits of error. It could be removed by postulating the existence of an isotope of hydrogen of mass 2, with a relative abundance $H^1/H^2=4500$. It should be possible, although difficult, to detect such an isotope by means of band spectra.

The above discussion shows that, with the exception of hydrogen, the new Mecke and Childs' abundance ratio gives a satisfactory agreement between the mass-spectrograph and the chemical results. The agreement is in fact somewhat better than that obtained with an assumed abundance ratio of 1250 to 1, or of 1070 to 1. The case of hydrogen, however, distinctly calls for further investigation.

Aston[11] has asked for suggestions as to the best basis for chemical atomic weights and atomic masses. We believe that the facts presented in this letter indicate that, from the experimental standpoint, the quantitative relation between the *mean* atomic weight of oxygen, and the mass of the atomic species O^{16} is rather uncertain at the present time, and is likely to remain so for the present. It should also be pointed out that there is as yet no *proof* that the relative abundance of the oxygen isotopes, in different sources, is strictly constant.[12] The possibility that the relative abundance is *not* constant is the most compelling argument for a change in the basis of the atomic-weight system. What that change should be can best be decided by chemists, but we believe that further data are needed before any change is seriously considered. The one point we wish to emphasize here is that there

[7] R. T. Birge, Phys. Rev. Supplement **1,** 1 (1929). See pp. 19–26 and 69.

[8] A. S. King and R. T. Birge, Astrophys. J. **72,** 19 (1930).

[9] G. P. Baxter and C. H. Greene, J. Am. Chem. Soc. **53,** 604 (1931).

[10] E. Moles and T. Batuecas, J. Chim. Phys. **17,** 539 (1919).

[11] F. W. Aston, Nature **126,** 953 (1930).

[12] The mass-spectrograph is perhaps the most reliable method for investigating this question.

now exist two systems for the measurement of atomic masses, connected by a relatively *uncertain* factor. For that reason it seems best, for the present, not to convert results obtained on one system into the other system, by the use of some assumed conversion factor.

R. T. BIRGE
D. H. MENZEL
University of California,
May 27, 1931.

The Masses of O^{17}

The writers have recently built a new accurate apparatus, in order to obtain, among other values, more exact masses for the nucleus of O^{17}, since they had concluded that additional data were needed in order to establish definite relations. Urey,[1] however, considers that the data already available demonstrate the existence of three quantum states for this nucleus.

The purpose of this letter is (1) to give, as a minor change, a different set of values for the ranges of the protons; (2) what is more important, to point out that while we do not disagree with Urey's conclusion above, it seems to us that the few available data should be classified in a slightly different way; (3) and to add a calculation, omitted by Urey, of an inelastic collision between an α-particle and a nitrogen atom as obtained by Harkins and Shadduck:[2]

The data given in this paper lead to the following calculated values:

TABLE I.

M_0 (nucleus)	M_0 (atom)	$\Delta M_1 \times 10^5$	$\Delta M_2 \times 10^5$
16.99891	17.00328	1	12

Here M_0 represents the rest mass of the oxygen, ΔM_1 is the error of M_0 introduced by a 1 percent error in the energy of the α-particle, and ΔM_2 that due to an error of 10′ in the angle ω between the track of the α-particle and that of the oxygen nucleus. In the calculation, the value 14.00800 (Aston) is taken as the rest mass of the nitrogen atom, as was presumably done also by Urey. The values are collected as follows:

TABLE II. *Mass of O^{17}.*

Track	M_0 (atom)		Average M_0 (atom)	
B4	17.00508	High level	17.00508	
				0.00189
B5	17.00330			
H+S 1	17.00328	Middle level	17.00319	
B3	17.00300			
				0.00171
B2	17.00148	Low level	17.00148	

The values differ somewhat from those of Urey, who omits track H+S 1.

We have excluded from this table the calculated values for the following four tracks as not having a sufficient bearing upon the division into the above three groups.

TABLE III.

Track	M_0 (atom)	Reason for rejection from Table II
H+S 3	17.0050	Agrees well with the value 17.00508 for the B4 track, but one of the pair of photographs of the event was not clear
B7	17.00402	Tracks curved (rejected by Urey)
B6	17.00293	Angle ω too small to give accuracy in M_0
B1	17.00370	Probably as accurate as those listed in Table II, but deviates too far from mean of other three in middle level to offer evidence in favor of the existence of this level

[1] Urey, Phys. Rev. (2) **37**, 923 (1931).

[2] Harkins and Shadduck, Proc. Nat. Acad. Sci. **12**, 707 (1926).

Thus, according to our classification,

(1) the lowest level is represented by only one value,

(2) the middle level by three values, and

(3) the high level by only one value.

The ranges of the protons emitted are given in Table IV. Urey assumes that the range varies as the cube of the initial velocity, but a closer approximation is probably given by use of the 3.5 power, as is done by Chadwick, Constable and Pollard.[3] On this basis, the ranges in cm at 15° and 760 mm are:

TABLE IV.

B4	B6	H+S 1	B3	B5	B1	B7	B2
17.3	18.8	20.4	25.0	25.0	31.9	38.6	59.7

Except for the highest values, this change of power does not give a great increase of range.

It may be noted that the values of ω, the angle between the extension of the track of the α-particle and that of the oxygen nucleus, is always small. The observed values are:

TABLE V.

B6	H+S 1	B4	B7	B3	B1	B5	B2
7° 54′	15° 21′	19° 24′	21°	21° 13′	22° 0′	22° 12′	28° 51′

This angle is always small because (1) the initial velocity of the proton is limited, (2) the mass of the oxygen is relatively high, and (3) no disintegration has as yet been observed with certainty by the photographic method were the velocity of the α-particle at impact is less than 1.83×10^9 cm per sec.

Some additional evidence for the validity of the three levels in the O^{17} nucleus seems to be given by the fact that the differences between the average masses are moderately nearly equal, as shown in Table II by the values 0.00189 and 0.00171. However, additional experimental evidence is needed for the definite determination of the energy levels.

WILLIAM D. HARKINS
DAVID M. GANS
University of Chicago,
May 21, 1931.

[3] Chadwick, Constable and Pollard, Proc. Roy. Soc. **A130,** 477 (1931).

The Electrical State of the Sun. A Correction

Dr. H. B. Maris of this laboratory has kindly brought to my attention an error in the above entitled paper (Phys. Rev. **37**, 983 (1931)) which effectively nullifies the paragraph containing arguments and calculations purporting to show that the sun is electrically neutral. In Eq. (3), Q represents the free electrical charge per unit length of the equivalent circuit rather than the total free electrical charge. On making the correction we find that, although other evidence indicates that the sun is electrically neutral, our magnetic calculation, alone, is quite incapable of establishing that fact.

The corrected calculated value of the galactic magnetic field according to Anderson's hypothesis of the annihilation of positive electrical charge is still so large (10^3 gauss) as to be impossible and our original conclusion is therefore unchanged. The incorrect assignment of the value of Q did not affect the detailed calculations in other sections of the paper.

ROSS GUNN
Naval Research Laboratory,
Bellevue, Anacostia, D. C.,
May 25, 1931.

ERRATA

RADIATION OF MULTIPOLES

By Karl F. Herzfeld
Department of Physics, The Johns Hopkins University

(Phys. Rev. **37**, 253, 1931)

In a paper which appeared under this title there are unfortunately some mistakes, the correct formulas are given below:

On page 256 the following formula (9)

$$\psi = \sum c_k \psi_k e^{-2\pi i k \nu t} \qquad \psi_k = e^{-\xi^2/2} H_k(\xi) b_k$$

Same page, before formula (10)

$$b_k = \left(2^{-k} \frac{1}{k!} \left(\frac{4\pi M \nu}{h}\right)^{1/2}\right)^{1/2}.$$

Instead of formula (16) on page 258

$$a_s^{(k)} = \frac{k!}{i!} 2^i (-1)^{(k-i)/2} \frac{1}{\left(\frac{k-i}{2}\right)!} \text{ for } k - i \text{ even.} \tag{16}$$

At the bottom of page 258 and on top of 259.

$$\begin{aligned} I_{k,s}^{(n)} &= 0 \text{ if } s - n \text{ odd} \\ &= \pi^{1/2} \sum_{j=0}^{(n-s)/2} \frac{(4j)!}{2^{4j}(2j)!} (2j + k + s) \cdots (2j + 1) \\ &\quad (-1)^{j+(s-n)/2} 2^{2j+k+s-n} k! \frac{1}{\left(\frac{n-s}{2} - j\right)!} \frac{1}{(2j + k + s - n)!} \\ &= \pi^{1/2} (-1)^{(s-n)/2} 2^{k+s-n} k! \sum_{j=0}^{q} (-1)^j \frac{(4j)!}{(2j)!^2} \frac{1}{4^j} (2j + k + s)! \\ &\quad \times \frac{1}{(q-j)!} \frac{1}{(2j + k - q)!} \end{aligned} \tag{17}$$

with $n - s = 2q$.

Finally for the formulas which occur in the middle of page 259

$$I_{k,2}^{(2)} = (\pi)^{1/2} 2^k k! \frac{(k+2)!}{(k!)} = (\pi)^{1/2} 2^k (k+2)!$$

If $n = 3$ (tetraeder) there are possible two transitions

$s = 1$, frequency ν

$$\begin{aligned} I_{k,1}^{(3)} &= -(\pi)^{1/2} 2^{k-2} k! \left\{ \frac{(k+1)!}{(k-1)!} - \frac{4!}{(2!)^2} \frac{1}{4} \frac{(k+3)!}{(k+1)!} \right\} \\ &= +(\pi)^{1/2} 2^{k-2} \left\{ \frac{3}{2}(k+2)(k+3) - k(k+1) \right\} k! \end{aligned}$$

$s = 3$ frequency 3ν

$$I_{k,3}^{(3)} = (\pi)^{1/2} 2^k \frac{k!(k+3)!}{k!} = (\pi)^{1/2} (k+3)! 2^k.$$

In general, we have for $s = n$, frequency $n\nu$

$$I_{kn}^{(n)} = (\pi)^{1/2} 2^k \frac{k!(k+s)!}{k!} = (\pi)^{1/2} 2^k (k+j)! \tag{18}$$

HYPERFINE STRUCTURE IN IONIZED BISMUTH

By Russell A. Fisher and S. Goudsmit
Department of Physics, University of Michigan

(Phys. Rev. **37,** 1057, 1931)

The photograph of the hyperfine structure of Bi II 4705 (Fig. 2b) was unfortunately inverted. The complete Fig. 2 should appear as follows:

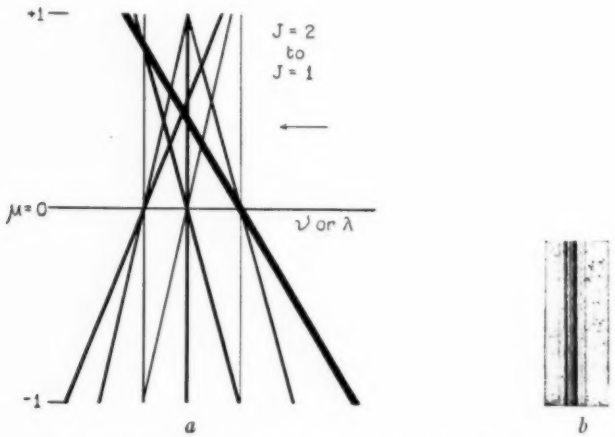

Fig. 2. Diagram for transition $J=2$ to $J=1$ compared with Bi II λ4705. $\mu=+0.457$, tota $\Delta\nu=2.71$ cm^{-1}. The arrow indicates where the line pattern fits the diagram.

THE SCATTERING OF UNPOLARIZED X-RAYS

By G. E. M. Jauncey and G. G. Harvey
Washington University, St. Louis, Missouri

(Phys. Rev. **37,** 698, 1931)

The denominator of the right side of Eq. (12) should be raised to the fourth power. The corrected equation is

$$I_{atom}=4I_e/(1+0.022x^2)^4 \qquad (12)$$

SURFACE TENSION OF MERCURY

By Marie Kernaghan
Department of Physics, The Saint Louis University

(Phys. Rev. **37,** 990, 1931)

The ordinate of Fig. 3 should read "Surface tension (dynes) Corrected values".

BOOK REVIEWS

Veröffentlichungen Des Wissenschaftlichen Zentral-Laboratoriums der Photographischen Abteilung-Agfa- Band I. Pp. 155, figs. 94. S. Hirzel, Leipzig, 1930. Price RM10.

The photographic division (Agfa) of the I. G. Farben industrie has inaugurated an annual publication in which the results of technical and theoretical photographic investigations of that laboratory are gathered together. In general each volume will consist both of articles which have appeared in other places and of some which have not been previously published. The annual should prove a great benefit to the photographic research world by helping to keep important photographic knowledge collected.

The first volume contains an article on the existing theories of the latent image, several papers on sensitometry with special reference to color sensitivity, an announcement of new sensitizers for the extreme red and infrared photography. An article on the testing of sound film is particularly good in that clear and complete picture of the physical problems involved in photographic sound recording is given. Articles on x-ray photography and on cellulose and its derivatives complete the volume. M. E. RUSSELL

Molecular Spectra in Gases. Report of the Committee on Radiation in Gases and Bulletin 57 of the National Research Council. E. C. KEMBLE, R. T. BIRGE, W. F. COLBY, F. W. LOOMIS, L. PAGE. Second printing 1930. Pp. 366. Price $3.50 (paper binding).

This bulletin originally issued in December 1926 has been reprinted with minor corrections and the addition of an index. Separate copies of the index are available for distribution.
E. C. KEMBLE

An Outline of Wave Mechanics. N. F. MOTT. Pp. 156, figs. 21. The Macmillan Company, New York, 1930. Price $2.80.

New sciences are complicated when they start, and grow simpler as we understand them better. Wave mechanics is no exception. The first papers, the first books, on the subject were mathematics and not much else. But now, with increased understanding, it is possible to dispense with more and more of the detail, and yet to become continually clearer and more comprehensible. Mott's admirable little book is an excellent illustration of this tendency. To the reviewer it seems singularly successful in its attempt to present enough detail to enable the principles of the subject to be accurately understood, and yet not enough to burden the reader. After reading it, one does not have the too common feeling that it could not be understood except by one who knew the whole subject beforehand.

It should not be supposed that Mott's book is intended for the general reader. It is distinctly for physicists, advanced students and research workers. It presupposes a considerable background of physics and mathematics. But it can honestly be recommended, for example, to the experimental physicists who want some idea of wave mechanics. The examples and illustrations are of a physical sort, and of a remarkable variety for such a small book. Particularly good, as one would expect from Mott's research, are the sections on collisions, scattering and such problems. Questions of stationary states, of atomic and molecular structure, are treated, but not in any great detail, as must be obvious from the small compass of the book. No problems, of course, are carried through in a complete manner, and yet one feels that the fundamentals are so adequately presented that the reader will be set thinking along the right line. As an elementary and readable account of wave mechanics, the reviewer feels that the book can be highly recommended. An idea of the actual contents can be obtained from the chapter headings: Waves and Particles, The Wave Equation, Group Velocity and the Uncertainty Principle, The Theory of Stationary State, The Absorption of Radiation, The Helium Atom and the Hydrogen Molecule, Dynamics of Systems containing many Electrons, The Spin of the Electron and the Exclusion Principle. J. C. SLATER

Principles of Electrical Engineering (Second Edition). W. H. TIMBIE AND V. BUSH. Pp. 595, figs. 270. John Wiley and Sons, New York, 1930. Price $4.50.

We regret that in the review of this book which appeared in the May 15 issue of this journal, page 1374, the name of the publisher was erroneously given.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE WASHINGTON MEETING, APRIL 30, MAY 1 AND 2, 1931

The 170th regular meeting of the American Physical Society was held in Washington, D.C., at the Bureau of Standards on Thursday and Friday, April 30 and May 1, and at the National Academy of Sciences on Saturday, May 2, 1931. The first session began at ten o'clock on Thursday morning. The presiding officers were W. F. G. Swann, President of the Society, Paul D. Foote, Vice-president, Joseph A. Becker, Lyman J. Briggs, Arthur H. Compton, Karl K. Darrow, Henry G. Gale, Enoch Karrer and L. P. Sieg. At the Bureau of Standards on the first and second days of the meeting the registration was 388. A fair estimate of the total attendance at the sessions was between four and five hundred.

On Thursday afternoon the Society omitted its regular sessions from one-thirty to three-thirty o'clock to meet with the newly formed American Association of Physics Teachers. At this session Dr. A. W. Hull of the General Electric Company presented an invited address on "Qualifications of a Research Physicist."

On Thursday evening a public forum was called at the National Academy Building to discuss methods of promoting interest in all branches of physics. This meeting was called by L. W. McKeehan, chairman of the Committee on Sections and was presided over by F. K. Richtmyer.

On Friday evening the Society held a dinner at the Hotel Washington. The President presided at this dinner and the after-dinner speakers were George K. Burgess, Arthur H. Compton, Charles Darwin and F. Henning. R. H. Fowler was also a guest of the Society at the speakers table. The attendance at this dinner was 243.

On Saturday afternoon at the National Academy Building there was held a special colloid program. The papers at this session were invited. The presiding officer of this meeting was Enoch Karrer of the B. F. Goodrich Company.

Meeting of the Council. At its meeting held on Thursday, April 30, 1931, sixteen persons were transferred from membership to fellowship and thirty-seven were elected to membership. *Transferred from Membership to Fellowship:* James H. Bartlett, Jr., David G. Bourgin, V. L. Chrisler, S. Goudsmit, Robert J. Havighurst, Paul Kirkpatrick, W. W. Nicholas, Linus Pauling, Shirley L. Quimby, Richard Ruedy, A. G. Shenstone, Ernest C. G. Stückelberg, George E. Uhlenbeck, N. H. Williams, Mark W. Zemansky and R. V. Zumstein. *Elected to Membership:* Edward B. Baker, M. C. Banca, William E. Berkey, Margaret F. Blackford, Robert L. Boyer, Percy H. Carr, Nickola

Chako, Thomas A. Elkins, David W. Epstein, Richard Evans, O. Rex Ford, Gladys M. Francis, Garret A. Hobart 3rd, Cleveland B. Hollabaugh, Howard B. Holroyd, Jun Koana, C. M. Lewis, Walter G. Marburger, A. T. McPherson, Paul C. Mitchell, George C. Munro, Robert J. K. Murray, Leon S. Nergaard, Paul A. Northrop, Syoten Oka, Allan E. Parker, Clifford M. Potter, Norman A. Shepard, William B. Shockley, Leland B. Snoddy, Daniel S. Stevens, G. R. Tatum, Sigeo Uneno, Forrest Western, John A. Wheeler, E. P. Wigner and Robert L. Womer.

The regular scientific program of the Society consisted of 163 papers, numbers 11, 25, 34, 40, 44, 47, 48, 49, 50, 68, 71, 95, 108, 120, 127, 131, 144, 152, 153, 155, 157, 158 and 163 were read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

1. Dissociation of water vapor in electrical discharge. ERNEST G. LINDER, *Cornell University.*—By use of Townsend's ionization equation and Aston's result for the potential distribution in the Crookes dark space, the number of electrons produced at each point in the dark space can be obtained. From this, may be calculated the total energy of all the electrons generated by each primary electron, i.e., $\int_0^S (V_1 - V)dn$, where S = length of dark space, V_1 = cathode potential drop, V = space potential, n = number of electrons. Using experimental values of S and V_1 and Townsend's constants, it is thus found that for discharge currents of 1–25 m.a. the average energy per electron runs from 53.8 to 79.2 volts, these values being from 17.8 to 14 3 percent of the corresponding total cathode drop energies The amount of dissociation in the dark space and negative glow for the above currents is from 4.78 to 5.90 molecules of water per electron, which gives an almost constant value of 11 volts per dissociation. The results suggest that dissociation is due to excitation of the molecule. Probe measurements in the positive column give an electron density of 7.4×10^7 electrons per cm^3, and a mean energy of 3.71 volts. If a probability of dissociation by electron impact equal to 0.0024 be assumed, the dissociation in the positive column can be accounted for.

2. The electro-optical shutter and spark breakdown. FRANK G. DUNNINGTON, *University of California.* (*Introduced by Ernest O. Lawrence*).—The use of the electro-optical shutter in investigations of rapidly varying phenomena necessitates knowledge regarding its manner of functioning and limitations. Using a typical experimental set-up as an example, theoretical cut-off curves have been calculated: 1st, assuming an instantaneous drop of the controlling voltage (i.e. spark gap), and 2nd, assuming the controlling voltage decays according to a definite law. These indicate an effective cut-off time (90% to 10% transmission) of from 2.5 to 4×10^{-9} sec. and a total lag of 4 to 9×10^{-9} sec. Experimental results show a complete change in the appearance of the spark in 5×10^{-9} sec., thus indicating an effective cut-off time somewhat less than this value. Other results set a lower limit on the total lag of about 7×10^{-9} sec. The effective working of the shutter is dependent on the following major factors: (1) purity of nitrobenzene used in Kerr cell; (2) resistance of leads to cell; (3) voltage applied; (4) capacity of cell; (5) steepness of voltage wave used to control shutter. Contrary to previous beliefs, theory and experiment show the best control voltage is only slightly under that giving 100% transmission. A graphical survey giving the step by step development of the breakdown of a gap in an initially homogeneous field has been made for pressures from 20 to 76 cm and gap lengths from 1 to 10 mm.

3. The effect of pressure on the rate of fall of potential in condensed discharges. J. C. STREET AND J. W. BEAMS, *University of Virginia.*—The experimental method was essentially the same as one recently described (Street, Bulletin American Phys. Soc. Feb. 1931) and somewhat similar to Toepler's (Archiv für Elektrot. **14,** 305, 1925) though different in important essentials. Electrical impulses produced by the discharge under investigation traveled along two

parallel symmetrical lead wires to their open ends where they were reflected. The maximum potential across the two ends when measured as a function of the length of lead wires gave a curve from which the rate of fall of potential across the discharge was determined. Our results show that in the first part of the breakdown the resistance can best be represented as a function which decreases exponentially with time. When the potential was very slowly applied (static breakdown) the following are some of the results obtained for the decrease of potential with time:

Pressure in cm of Hg	Time of fall from 100 to 20%
38	4.7×10^{-8} sec.
54	2.5
75	1.7
95	1.1
115	.8
139	.8

The results are in general accord with the calculations of Schilling (Archiv für Elektrot. **25**, 97, 1931). Incidentally they indicate how to obtain a maximum rate of discharge for Kerr cells and illustrate how they are damped when used with short leads.

4. On the formation of an arc or spark on interrupting an electric circuit. THOMAS J. KILLIAN, *Massachusetts Institute of Technology.*—There seem to be two possible sources of the spark or arc which results when a physical circuit, carrying unidirectional current, is opened. J. Slepian (J.A.I.E.E., Oct., 1926) has suggested that the initial ionization is due to the temperature rise of the last contact point of the separating electrodes. At high breaking speeds this theory is subject to certain theoretical and experimental difficulties. If no conduction current flows immediately after the contacts are opened the charging current will cause the potential difference and the electric intensity between the contacts to increase. It is shown that the electric field may attain 10^6 to 10^7 volts cm^{-1} at which values "field" currents may flow. When the potential difference between the electrodes is such that the electrons, which have been drawn from the metal by these intense fields, may produce ionization an arc or spark results. An analysis of oscillograms taken at various current densities and opening speeds seems to show that this mechanism may initiate the discharge. This may indicate a method of studying "field" currents at high densities which until now have only been studied at extremely low densities.

5. Vacuum spark discharge. L. B. SNODDY, *General Electric Co.* (*Introduced by A. W. Hull.*)—Impulsive breakdown between pure copper electrodes in high vacuum has been investigated by means of the cathode ray oscillograph and the rotating mirror. (See J. W. Beams, Review of Scientific Inst. **1**, 667, 1930). The mirror photographs of the discharge show a luminous spot at the anode lasting from 1 to 4×10^{-7} sec. and luminosity at the cathode starting slightly later (1 to 2×10^{-7} sec.) than that at the anode and continuing throughout the discharge. The anode does not remain luminous unless the current is very large. The breakdown has two stages; the first a pure electron discharge, lasting less than 5×10^{-7} sec., followed by a low voltage copper vapor arc. The volt-ampere characteristic of the high voltage stage follows the well known law for auto-electronic emission. From the volt-ampere curves the area of emission at the cathode can be computed (Stern, Gossling and Fowler, Proc. Royal. Soc. **124**, 699, 1929). For two gaps investigated the areas were approximately 3×10^{-3} $\overline{cm}^2$ and 1×10^{-5} $\overline{cm}^2$. Using these areas and the rate of potential rise as determined by the oscillograph it is shown that in each case the anode spot at the time of breakdown reaches a temperature of approximately 2600°C. Photomicrographs of the anode show craters of area agreeing well with the computed areas. Current densities, determined from the circuit constants and measured areas of the cathode craters, range from 10^8 amps/$\overline{cm}^2$, at 5×10^{-7} sec. after breakdown, to 8×10^3 amp/$\overline{cm}^2$, at which value the arc goes out.

6. On the temperature of cathode in vacuum arc. R. TANBERG AND W. E. BERKEY, *Westinghouse Elec. & Mfg. Co., East Pittsburgh.* (*Introduced by Thomas Spooner.*)—Pyrometric and spectroscopic tests show that the metal cathode spot in a vacuum arc is not at an extremely high temperature. The temperature of a copper cathode is measured by an optical pyrometer and found to be about 3000°K in a 20 ampere arc. Spectroscopic examination of the cathode spot shows only a faint continuous spectrum indicating that the temperature of the cathode is not high. A temperature of the above magnitude is shown to be sufficient to give the rate of vaporization required under extreme assumptions. The results show that the high speed of the vapor stream issuing from the cathode region cannot be due to high temperature of the cathode itself.

7. The cathode fall of an arc. R. C. MASON, *Westinghouse Elec. & Mfg. Co., East Pittsburgh.*—To explain the mechanism of a mercury-pool arc, in which the cathode is at a relatively low temperature, Langmuir has suggested that electrons are extracted from the cathode by a very high field. Presumably, the same theory will apply to all arcs in which the cathode is not hot enough for appreciable thermionic emission. An analysis is presented in this paper showing that, under the same conditions, an arc in which the high field is operative should have a cathode fall several volts greater than an arc with a thermionic cathode. Upon either the classical Schottky theory, or the quantum mechanical theory of high field emission, the energies of electrons at the boundary of the cathode fall space will be several volts less in the high field arc than in the thermionic arc; so, to produce sufficient positive ions for space charge purposes, the cathode fall of the former must be greater than that of the latter. A test is thus suggested for the Langmuir theory of an arc.

8. Measurements on the vapor stream from the cathode of a vacuum arc. W. E. BERKEY AND R. C. MASON, *Westinghouse Elec. & Mfg. Co., East Pittsburgh.*—The velocity of the vapor stream issuing from the cathode region of a vacuum arc between copper electrodes is calculated from (1) the energy received by a vane 3 cm in front of the cathode, as measured by the rate of rise of temperature; (2) the momentum imparted to the vane, as determined by the deflection of the vane. The mass used in the calculations is that of the copper deposited on the vane. The average velocity of the vapor, computed from data obtained by either method, is over 10^6 cm per second, confirming Tanberg's momentum measurements. There is some evidence that the vapor is ionized to a considerable degree. Radiation from the arc, or energy of recombination on the vane, can account for only a small part of the total energy received by the vane.

9. A method for the comparison of magnetic susceptibilities of feebly magnetic salts. L. G. HECTOR AND ALBIN N. BENSON, *The University of Buffalo.*—A method depending upon induced current phenomena may be employed for comparing the magnetic susceptibilities of substances whose electrical conductivity is small. The present method depends upon the comparison of the alternating electromotive forces developed in two coils each of which is coupled to a field coil. A tube filled with the salt to be examined is then placed in one of the pick-up coils and a change in the coupling between the pick-up coil and the field coil is thereby produced. By means of a variable resistor shunted about one field coil a balance between the induced e.m.f. is restored. Comparison of the two induced alternating e.m.f. was first attempted by means of a vacuum tube voltmeter, but slight irregularities in wave form and shifts in phase resulted in uncertainty in the readings. In the latest method, current from each pick-up coil is rectified by thermionic tubes and the rectified current is further smoothed out by filters. The potentials developed across the last condenser bank in each filter are then compared by means of a direct current galvanometer.

10. Block structure and magnetic viscosity. FRANCIS BITTER, *Westinghouse Elec. & Mfg. Co., East Pittsburgh.*—As a result of the work of Becker (Zeits. f. Physik **62,** 253, 1930) and Powell (Proc. Roy. Soc. **130,** 167, 1930) it is now possible to write the expression for the potential energy of a single crystal as a function of the direction of magnetization in the crystal, say $\Phi(\theta, H)$. This expression depends on the crystalline field, or (s, l) interaction, and on the distortion of the lattice, and has, in general, several minima as a function of θ. If the crystal is made up of regions of spontaneous magnetization, the equilibrium distribution of orientations is

given by an expression of the form exp. $(-\Phi_v(\theta, H)/KT)$ where Φ_v represents the potential energy of such a region. This distribution cannot in general be established in a reasonable time because of the existence of several maxima of Φ_v. If, however, we know the distribution of orientations, f, at a time $t=0$ (say complete demagnetization, or saturation) then the distribution at a time t resulting from a change in H is given by the diffusion equation

$$a\nabla\cdot(f\nabla\Phi_v) + b\nabla^2 f = \partial f/\partial t.$$

This equation has not been solved except for special and simple forms of Φ_v. A closer inspection, however, shows that a gradual "creeping" of magnetization will not, in general, occur unless the depth of the Φ_v minima is comparable with KT. Since the depth of these minima depends on the volume of a region, magnetic viscosity phenomena in single crystals may eventually be used to determine the volume of the regions of spontaneous magnetization and so check the hypothesis (Phys. Rev. **37**, 91, (1931)) that they are identical with Zwicky's blocks.

11. Magnetic properties of magnetite crystals at low temperature. CHING-HSIEN LI, *University of Illinois.*—Thin circular plates cut parallel to the 100, 110, and 111 planes of the magnetite crystal were prepared. Both the perpendicular and parallel components of magnetisation at low temperatures down to that of liquid air were investigated by the method of torsion. It was found that the magnetic property of the crystal was abruptly changed at about -160 degrees centigrade. It seems that the elementary magnetic elements within the crystal are very easily rotated in the magnetic field at that particular temperature. This particular temperature corresponds exactly to the temperature at which the heat capacity of magnetite is suddenly increased to a maximum point as was found experimently by R. W. Millar two years ago. Weiss' theory of the molecular field as applied to this change of specific heat and the corresponding change of magnetic property is in the process of investigation.

12. Effect of heating on residual magnetism. R. L. SANFORD, *Bureau of Standards, Washington, D. C.*—Experiments with a 0.63 percent carbon steel show that if the structure is lamellar pearlite, consisting of alternate plates of iron and iron carbide, the residual induction reverses sign at a temperature of approximately 200°C and regains part of the magnetization in the original direction upon cooling. If the temperature is raised to 800°C, the residual induction disappears and does not reappear on cooling. If the material is remagnetized in the original direction while at a temperature of approximately 265°C, the residual induction decreases upon cooling and finally reverses at a temperature of about 30°C. Hardened steel does not reverse but the presence of very fine lamellar pearlite produces a reversal. Precipitated carbide produced by reheating a hardened specimen does not cause the reversal. The lamellar structure appears to be necessary for the reversal. The first reversal can be satisfactorily explained as the result of the thermomagnetic transformation of the carbide plates which first reverse the magnetization in the adjacent iron plates and then become nonmagnetic at the so-called A_0 point. The reversal after remagnetization at the high temperature is not so easy to explain.

13. Annual variations in magnetic storms. H. B. MARIS, *Naval Research Laboratory, Bellevue, Anacostia, D. C.*—A new list of magnetic storms for the years 1839 to 1930 shows an annual variation in the frequency of disturbances with two equal maxima about a week following the equinoxes and two equal minima at the solstices. The ratio of the maximum to the minimum frequency is nearly two to one. The distribution of frequency F is given approximately by the equation, $F=k(3+\cos 2\theta)$, where θ is the position of the sun on the ecliptic. Three groups of storms showing annual recurrence interrupt the normal distribution curve. The first, 1840 to 1865 had a maximum about February 20, the second group started April 10, 1854, and was intermittently persistant with a two year period till 1875 and the third group started May 16, 1913, and is almost unbroken since then. The change from maximum to minimum frequency between equinox and solstice is explained as the result of three effects. The ultraviolet flair, which is assumed to come from the solar latitude where sun-spots are observed, should increase in intensity as the earth increases its solar latitude. This would be expected to give a ten percent change in storm intensity. Expansion of the upper atmosphere as it is heated by the solar flair causing the storm will move the conducting Heaviside layer across the earth's magnetic field with a dynamo effect which will decrease by about fifteen percent from equinox to solstice.

Winds blowing from day toward night will have a maximum dynamo effect in driving atmospheric electric currents at equinox.

14. Magnetic properties of copper-nickel alloys. E. H. WILLIAMS, *University of Illinois.*—The magnetic susceptibility of alloys of copper and nickel in proportions ranging from 0.1 to 70 percent nickel have been studied. Although copper is only weakly diamagnetic it requires 0.8 or 0.9 percent nickel to neutralize this diamagnetic effect and 56 percent nickel is required before the alloy shows ferromagnetic properties at ordinary temperatures. For amounts of nickel from one percent up to 30 percent the alloy, while paramagnetic in most respect, does not obey any law of paramagnetism with regard to temperature. As the temperature is increased the susceptibility first increases and then decreases, the maximum occurring in the neighborhood of the Curie point for nickel. In the case of alloys containing more than 30 percent nickel the susceptibility decreases with increase of temperature for temperatures above 20°C. So far as the phenomena of increasing paramagnetic susceptibility are concerned there is at present no explanation. It has been suggested that a few atoms or molecules of nickel do not lose their magnetic identity in the alloy and that these atoms with their spinning electrons become more mobile as the temperature is increased. One objection to this is that the susceptibility is independent of the field.

15. The origin of thermionic electrons from oxide coated filaments, R. W. SEARS AND J. A. BECKER, *Bell Telephone Laboratories, Inc.*—The following experiments show that the emission is determined by the condition of the oxide surface and not the core-metal surface as proposed recently by Lowry (Phys. Rev. **35,** 1367, (1930)) and also Riemann and Murgoci (Phil. Mag. **9,** 440, 1930). (1) When barium is deposited on the oxide surface either by evaporation from an external source or by electrolysis of the oxide itself, the emission changes even though the temperature is so low that the barium could not diffuse to the core surface. (2). A removal of the oxide coating while the filament is at room temperature causes the emission as determined at low temperatures, to decrease by a factor of 6000 or more. (3). When space charge limited current is drawn to a plate, the potential of a point in the oxide is always positive with respect to the core surface by an amount directly proportional to the current. If the current were determined by the core surface this potential should be negative and should not vary linearly with the current. The experimental facts adduced to prove a limitation by the core surface are not conclusive and can be explained on the view proposed here.

16. Theoretical interpretation of experimental Richardson plots. W. H. BRATTAIN AND J. A. BECKER, *Bell Telephone Laboratories, Inc., New York.*—The theoretical equation for the saturation current is

$$\ln i - 2\ln T = \ln A + \int_1^T \frac{b}{T^2}dT - (b)_{T=1} = \ln A - \frac{a}{T} \qquad (1)$$

$A = 4(1-r)\pi mk^2e/h^3$, "b" is defined in terms of L_p, the total heat of evaporation per mole at constant pressure. $b = (L_p/R) - (5T/2)$ "a" is defined by Eq. (1). It is related to the free energy If "a" and "b" are functions of T, an experimental plot of $\ln i - 2\ln T$ vs. $1/T$ will, in general, not be a perfect straight line. At any value of $1/T$ a tangent can be drawn. Its slope is $-b$ or $[-a + T\,da/dT]$ and the intercept is $[\ln A - da/dT]$ or $[\ln A + (b-a)/T]$. Actually, db/dT is usually so small that the mean straight line through the experimental points is practically coincident with the tangent at the mean value of $1/T$. If, as Herzfeld suggests, "a" $= h\nu_0/k$; the slope of the Richardson plot equals $-(h/k)[\nu_0 - T\,d\nu_0/dT]$ where the slope, ν_0, and $d\nu_0/dT$ all refer to values taken at the same temperature; the logarithm of the universal constant A is equal to the intercept $+(h/k)(d\nu_0/dT)$; also, the term "work function" cannot, in general, be used for both the slope of the Richardson plot and $h\nu_0$.

17. Influence of space charge on current fluctuations. E. W. THATCHER AND N. H. WILLIAMS, *University of Michigan.*—Current fluctuations of two fundamental types are recognized in a circuit containing a thermionic element: (1) Those due to the discreteness of the carriers, governed by probability relations applied to their departure from the cathode and collection at the anode. (2) Those due to thermal agitation of electricity in the circuit, analogous

to the Brownian fluctuation of particles in colloidal suspension. The influence of electron space charge on these fluctuations has been investigated with especially designed tubes. Precise measurements in this region have hitherto been unattainable on account of the inherent "mixed" nature of the emission from metal surfaces. Abnormalities arising from this source in tungsten and thoriated tungsten have been studied and controlled. A new treatment of the shot effect as applied to pure electron emission yields an expression for the ratio of the mean square value of the fluctuation voltage under given space charge conditions to that under strict temperature limitation of the current:

$$\frac{\bar{V}_s^2}{\bar{V}_i^2} = f(i_0/i)e^{-\omega^2/2\alpha^2}$$

I_0 is the space current, i the saturation current associated with a particular emitter temperature, and their ratio characterizes the space charge situation. The influence of the frequency term has been shown to be vanishingly small over a range of frequencies from 50,000 pps. to 500,000 pps. The function "f" has been experimentally determined for various situations of current limitation.

18. Supersonic satellites. W. H. PIELEMEIER, *Pennsylvania State College.*—As the path length in a Pierce acoustic interferometer was increased, satellites, or minor peaks, became more prominent in the curves which correlate the *excess of plate current over bias current* $(I_p - I_B)$, and the *mirror position*, (x). With the exception of the satellites these curves have a striking resemblance to the curves which correlate the *calculated square of the pressure amplitude in the air at the crystal surface* and the *mirror position*. A wave velocity independent of intensity was assumed for the calculation. If it is assumed that the velocity of the waves decreases to the imiting value, $V=(\gamma p/d)^{1/2}$, with diminishing intensity, not only the shape of the satellites, but also their position is thereby explained. Measurements were made with several crystals. For each of the frequencies tested the acoustic velocity as determined by the satellite positions differed by less than 0.06 percent from the above limiting value. In every case the velocity, as determined by the major peaks, *exceeds* the theoretical value by more than 0.5 percent. Such a large shift could scarcely be a frequency shift as the resonance positions are approached.

19. Canonical transformations and the vibrations of a loaded string. R. B. LINDSAY, *Brown University.*—The classical method of discussing the transverse motion of a finite string of negligible weight fastened at the ends with tension τ and loaded with particles of equal mass m and equally spaced at distances a is that in which the Lagrangian equations for a system of n degrees of freedom are set up and integrated by means of determinant analysis. It is here shown that if we denote the coordinate and conjugate momentum of the sth particle by q_s, p_s and perform the transformation to the new system Q_s, P_s defined by the transformation function

$$S = \sum_{k=1}^{n}(m/2)^2\omega_k^2 \cot Q_k\left[\sum_{s=1}^{n}a_{sk}q_s\right]^2,$$

where $a_{sk}=2\sin(sk\pi/n+1)/(m(n+1)\omega_k)^{1/2}$ and the ω_k form a set of parameters, the Hamiltonian

$$H = 1/2m\cdot\sum_{k=1}^{n}p_k^2 + \tau/2a\cdot\sum_{k=1}^{n+1}(q_k - q_{k-1})^2$$

(with $q_0=q_{n+1}=0$) transforms into $K=\sum_{k=1}^{n}\omega_k P_k$ with $\omega_k=2(\tau/ma)^{.1/2}\cdot\sin k\pi/2(n+1)$. The canonical equations now lead to $P_k=\text{const}$, $Q_k=\omega_k t+\beta_k$ and the usual solution is at once obtained from $p_k=\partial S/\partial q_k$ in the form

$$q_s = \sum_{k=1}^{n}a_{sk}P_k^{1/2}\sin(\omega_k t + \beta_k)$$

$$p_s = m\sum_{k=1}^{n}\omega_k a_{sk}P_k^{1/2}\cos(\omega_k t + \beta_k) \quad \text{where}$$

the ω_k appear as the characteristic frequencies (multiplied by 2π). The generalization to the continuous string is immediate. The transformation $q(x)=2/M^{1/2}\cdot\sum_{k=1}^{\infty}(P_k/\omega_k)^{1/2}\sin Q_k\cdot$

sin $k\pi x/l$ where l is the length and M the mass of the whole string, carries the Hamiltonian functional into $H=\sum_{k=1}^{\infty}\omega_k P_k$ where now $\omega_k=k\pi(\tau/Ml)^{1/2}$. The energy fluctuation and quantization of the loaded and continuous strings are investigated.

20. The elastic constants and the thermal expansion of a sample of rubber between room temperature and −30°C. W. W. STIFLER, *Amherst College*, AND PAUL C. MITCHELL, *Missouri Valley College.*—A method has been developed by which the coefficient of linear expansion, Young's modulus, and the coefficient of rigidity can be measured on the same sample of rubber at any temperature from that of the room down to −30°C. For a particular sample, the thermal expansion proceeds quite regularly in this range but the coefficients of elasticity increase rapidly as the temperature is lowered. For example, at 22°C, Young's modulus is 1.30×10^8 dynes per cm² and at −30°C it is 3.56×10^8 dynes per cm.²

21. Columns with variable end restraints. L. B. TUCKERMAN AND WM. R. OSGOOD, *Bureau of Standards.*—Because of its importance in aircraft construction, the Bureau of Aeronautics of the United States Navy has supported an investigation of the strength of columns with variable elastic end restraints, the investigation covering the range of lengths for which the failure is partly elastic and partly plastic. A theoretical analysis led to the conclusion that satisfactory corrections could be made for a rigid end mounting, which greatly simplified the test apparatus. The test results are found to be expressed advantageously in terms of the dimensionless variables

$$\sigma = P/(FcA), \quad \lambda = [l/(\pi r)](F_c/E)^{1/2}, \quad \kappa = [(2K)/(Pl)] + 2s/l,$$

where P = the maximum axial load which can be carried by the column. A = the cross-sectional area of the column, F_c = the short-column strength of the material, E = the modulus of elasticity of the material, l = the length of the column, r = the radius of gyration of the cross-section with reference to the gravity axis perpendicular to the plane of bending, K = the coefficient representing the end restraint, s = the length of the rigid portion at each end of the column. The dimensionless variables σ, λ, and κ render comparable test results on materials with different but affine stress-strain curves. Only by the use of these variables has it been found possible to coordinate all the test results which have been obtained. The variables λ and σ have been used previously in other column investigations. (L. B. Tuckerman, S. N. Petrenko, and C. D. Johnson, "Strength of Tubing under Combined Axial and Transverse Loading," N.A.C.A. Technical Note No. 307, pp. 3, 4, June, 1929.)

22. Methods for measuring the coefficient of restitution. LYMAN J. BRIGGS, *Bureau of Standards.*—A comparison is made of the following methods for determining the coefficient of restitution of elastic spheres, such as golf balls, when subjected to large deformations: 1. Ballistic method, in which the ball is struck by a flat-nosed projectile, and ball and projectile are caught in separate ballistic pendulums (Thomas). 2. Normal rebound of a ball dropped from a known height onto a massive flat plate, correction being made for air resistance during both fall and rebound. 3. Photographic method, in which the relative speed of ball and projectile after impact is determined from two spark photographs. 4. Rebound from a smooth inclined plate, involving measurement of the angles of incidence and reflection.

23. Velocity of sound in metal rods by a resonance method. LEHMAN C. SHUGART, *Lehigh University* (*Introduced by C. C. Bidwell.*)—A small coil is fastened to the end of the test rod and placed in a strong radial magnetic field. The coil is connected to the output of an audio-frequency oscillator. To the other end of the rod is fastened a carbon microphone button. At resonance frequencies corresponding to the fundamental or any overtone of the rod very sharp peaks are obtained in the microphone current. A correction must be made for the effective length of the rod due to the attachment of the driving coil and the microphone button. To get this correction, observation of the first overtone for a rod of twice the original length is made. The slight change in frequency enables the computation of the effective length. The equation is $v=2nl+4\Delta nl$. Value of velocity of sound for brass, steel and aluminum check very closely with the best published data. The method is being used for the determination of values in other

materials where data are lacking and especially for liquid metals. These may be contained in thin steel tubes, the peak for the resonance frequency in the liquid being easily distinguishable from that for the steel tube.

24. The vibrations of a plate with fixed center. ROBERT CAMERON COLWELL, *West Virginia University.*—A Chladni plate clamped at the center is usually set in vibration by bowing it at the edges. The sand figures formed in this way have been known for many years. If, however, a mechanical oscillator actuated by a vacuum tube is applied at different points on the plate, many new figures are formed. A few of these will be shown and a brief mathematical treatment given.

25. The arc spectrum of nitrogen. O. E. ANDERSON AND K. R. MORE, *University of British Columbia.* (*Introduced by G. M. Shrum.*)—The arc spectrum of nitrogen has been excited with low voltage, hot cathode arcs in mixtures of nitrogen with helium, neon and argon. Duffendack and Wolfe (Phys. Rev. **34**, 409, 1929) have used helium for the excitation of this spectrum, but it has usually been assumed that the lines could not be excited in argon. Since in these experiments the lines were observed in argon with an intensity of the same order as with helium, it has been necessary to revise the usual explanation of the excitation processes. When currents of the order of 1.5 amperes were used, the best results were obtained with 0.1 mm of nitrogen in 1.5 mm of argon. The spectrum has been examined in the region 3400–6000A. As some of the weaker lines were obscured by the nitrogen band structure, which varied with the nature of the admixed gas, it has not been possible to show that all the lines excited by helium were present in the argon mixture. A comparison of the intensities of the lines carried out with a Moll registering microphotometer showed that the strong NI lines were as intense as the moderately intense argon lines.

26. Activation of N_2–Hg mixtures by illumination with light from a quartz Hg arc. B. L. SNAVELY AND LOUIS A. TURNER, *Princeton University.*—Illumination of a mixture of nitrogen and mercury (5 mm N_2, 0, 001 mm Hg) in a quartz bulb containing a 0.6 mil tungsten filament produces a lowering of the resistance of the filament if it is originally at 400°C. This is the same effect which Kenty and Turner (Phys. Rev., **32,** 799 (1928)) found to be produced by active nitrogen and is presumably attributable to atomic nitrogen. Apparently the excited mercury atoms activate the nitrogen in some way. The effect is obtained only with the water-cooled arc, showing that the absorption of the 2537 line is involved. The effect is not obtained in similar helium-mercury mixtures. Rough preliminary measurements indicate that the magnitude of the effect is proportional to the first power of the intensity of the light.

27. The dissociation of excited iodine molecules by collision with argon atoms. LOUIS A. TURNER AND E. W. SAMSON, *Princeton University.*—By means of the absorption of the resonance line of the iodine atom ($\lambda = 1830$A.) it has been shown that iodine atoms are produced upon illumination of an iodine-argon mixture (0.3 mm I_2, 5 cm A) with continuous light of wave-length greater than 5100A., from a carbon arc. Absorption of such light should produce excited iodine molecules and not lead to direct optical dissociation. Apparently the excited molecules dissociate upon collision with argon atoms, as we might infer from the quenching of the iodine fluorescence by argon, as observed by Franck and Wood.

28. On the excitation of continuous spectra by bombardment of gases and vapors with cathode-rays. WILLI M. COHN, *University of Berlin.* (*Introduced by Otto Glasser.*)—It has been observed that gases or vapors which are bombarded by cathode rays, will emit under certain conditions a blue light the spectrum of which is continuous and has a maximum of intensity (photographically determined) at 4500A. The spectrum has been observed from 6200 to 3000A. The spectra received are not dependent on the kind of the ions generated. The light emitted is not polarized, but x-rays are generated. A working hypothesis is given in which is shown that the emission of the continuous spectrum may be produced by a mechanism similar to that of the continuous x-ray "Bremsspectrum."

29. Continuous spectrum from tungsten bombarded by 800 volt electrons. LAURISTON S. TAYLOR, *Bureau of Standards.* (*Introduced by F. L. Mohler.*)—Foote, Meggers and Chenault have

reported a continuous spectrum from metals bombarded by 1000 volt electrons (J. O. S. A. 9, 541, 1924). Preliminary measurements have been made of the intensity distribution of this radiation in the ultraviolet, from tungsten at voltages from 500 to 1200. At 800 volts the intensity $J(\lambda)$ increases regularly with decreasing wave-length, being about 3 times greater at 2800A than at 3700A. Between 500 and 1200 volts, the intensity distribution remains much the same and the intensity increases 2-fold. These results may be subject to an uncertain correction for electrons striking the stem instead of the target face.

30. Radiation from metals bombarded by low speed electrons. F. L. MOHLER AND C. BOECKNER, *Bureau of Standards.*—A paper presented at the New York meeting (No. 28) describes continuous spectra emitted by metals bombarded by large electron currents at low voltage, using the metal in the form of a small probe surface in a caesium or helium discharge. Measurements have been made with Be, Al, Cu, Ag, W, Pt, and Th in caesium discharges. Above 5 volts all except Ag and Cu give a spectrum of nearly equal energy per unit wave-length range. Ag is abnormally bright for wave-lengths longer than 3300A and Cu has a minimum in the green and yellow. Absolute intensities remain of the same magnitude with the same exceptions. The curves of isochromatic intensity versus voltage are very different. For Ag the intensity increases almost linearly from the threshold to 10 volts and more slowly beyond; for W it increases at an accelerated rate to 7 volts, is nearly constant to 12 and increases beyond. The Al curve has a high maximum at 12 volts and increases again above 16 volts. These variations (notably the Al maximum) are more pronounced at shorter wave-lengths. The intensity differences between Ag and W remain qualitatively similar in Cs and He discharges.

31. The blue-green fluorescence of mercury vapor. PAUL D. FOOTE, ARTHUR E. RUARK AND R. L. CHENAULT, *Gulf Research Laboratory and University of Pittsburgh.*—Visual photometric measurements were made on the blue-green fluorescence of Hg vapor excited only by the core of 2537. At the temperatures employed (21 and 33°C) the green glow cannot be seen in the absence of foreign gas. On adding a few millimeters of nitrogen to bring $^3P_1$ atoms down to $^3P_0$, it is bright. The intensity of the fluorescence increases to a maximum at 13 millimeters of nitrogen and then slowly fades as the pressure is increased. Using calibrated wire gauze screens to vary the intensity I of the exciting light, it was found that the fluorescent intensity J is definitely not a linear function of I. It obeys the equation $j+aj^{1/2}=bi$, where $j=J/J_0$ and $i=I/I_0$; J_0 and I_0 are the values obtained without screens; and a and b are constants for a given temperature and nitrogen pressure. Whatever be the molecule involved in the emission of the 4850 band, these experiments indicate that a $^3P_0$ atom is essential to its formation. The observed dependence of j on i can apparently be explained by assuming the active molecule contains two metastable atoms.

32. Direct measurement of τ. H. D. KOENIG AND A. ELLETT, *State University of Iowa.*—Ever since the well known experiments of Dunoyer (Le Radium **10**, 400, 1913) there has existed the interesting possibility of measuring the time between absorbtion and subsequent remission of radiation by an atom by observing the displacement taking place in this period because of thermal agitation. And it is equally well known that for such thermal velocities as are available in the laboratory the displacement in 10^{-8} secs. (the order of magnitude of the time usually involved) is too small to be measured. The depolarization of cadmium resonance radiation by very weak magnetic fields shows that τ for the 2^3P_1 state of Cd is unusually large. A beam of cadmium atoms was shot through a narrow perpendicular beam of λ3261 radiation. The illuminated part of the beam was screened from the camera. Atoms excited in the light beam and radiating after they had passed beyond the screen produced a blackening on the film densest just beyond the screen and perceptible for a distance of four millimeters. No blackening appeared below the screen showing that the spread above it was not due to secondary resonance. Photometer curves of the blackening are not yet available, but it is evident that τ is of the order of magnitude of 10^{-6} secs.

33. The average life for the line 2733A of ionized helium. LOUIS R. MAXWELL, *Bartol Research Foundation, Swarthmore, Pa.*—The line 2733A. (6→3) of ionized helium is made up of five lines (neglecting spin) whose average lives have been calculated according to the method of

Sugiura. The results obtained using Kupper's (amplitudes)^2 are: $6_1 \rightarrow 3_0$(2.59×10^{-9} sec.), $6_1 \rightarrow 3_2$ (2.59×10^{-9} sec.), $6_0 \rightarrow 3_1$ (9.06×10^{-9} sec.), $6_2 \rightarrow 3_2$ (1.52×10^{-8} sec.) and $6_2 \rightarrow 3_1$ (7.44×10^{-9} sec.). The experimental method used by the writer for determining the average life of excited ions has been applied to this line (2733A) and it is found to exhibit a displacement under the action of the transverse electric field which is slightly greater than would be calculated on the basis of the above values for the mean lives of the fine structure lines. This difference is probably caused by transitions into the sixth quantum state from higher excited states which would produce an apparent longer mean life and hence give too great an experimental displacement. However the experimental results obtained agree approximately with the above calculated values for the average life.

34. Mean life of the mercury line λ2537. PAUL H. GARRETT AND HAROLD W. WEBB, *Columbia University.*—The mean life of the mercury line λ2537 was measured by the alternating voltage method previously described (Phys. Rev. **24**, 113, (1924)). The radiation was excited in a quartz tube by impact with electrons from a hot cathode. The photoelectric system was contained in a separate tube also of quartz. The surface was zinc evaporated on a nickel plate. Measurements of the apparent life were made with diminishing mercury vapor pressures until further reduction of pressure produced no change in the measured rate of decay of the radiation. At these low pressures (below 3×10^{-4} mm for the geometry used) the absorption and re-emission of the radiation was negligible and the true life of a single excitation process was measured. This was found to be 1.08×10^{-7} sec. with an estimated precision of one percent.

35. Life of the nitrogen molecule in its first excited vibrational state. M. L. POOL, *Ohio State University.*—Curves showing the rate of decay of the metastable 2^3P_0 state of the mercury atom in a quartz resonance cell, containing carefully purified nitrogen at room temperature, are not accurately exponential. The rate of decay in the neighborhood of 10^{-4} sec. after terminating the optical excitation is more rapid than later. A high concentration of nitrogen molecules excited to the first vibrational state of the zero electronic state might be expected, due to collisions of the second kind with the 2^3P_1 state in mercury. It is assumed that in addition to usual diffusion and dissipative impacts with unexcited nitrogen, the decay of the number of metastable mercury atoms may be influenced by dissipative impacts with these excited nitrogen molecules whose number decreases with time by diffusion and by dissipative impacts. An equation for the number of metastable atoms is then obtained of the form $\exp\left[\alpha t + A(\exp \beta t - 1)\right]$. Evaluation of the constants from experimental data gives the following: Life of N_2 in first excited vibrational state, 1.2 to 1.9×10^{-4} sec. depending upon pressure; probability of dissipative impact, 1.5×10^{-4}; maximum life of 2^3P_0 state of Hg, 30×10^{-4} sec; probability of dissipative impact, 3.5×10^{-6}

36. High dispersion in the near infrared. J. D. HARDY, *National Research Fellow, University of Michigan.*—Using a Pfund type of spectrometer, with a five inch 1500 line grating and especially long focus mirrors, it has been possible to obtain an experimental resolving power of 20,000 in the region between one and two mu. Using the grating in the first order, the 10830A helium line was resolved into two distinct components, of separation 1.1A. The effective slit-width in the 1.5μ region could be made as small as 0.2A and due to the excellence of the optical system the grating remained completely filled with light. Several other helium doublets have been resolved and the relative intensity of the two components compared. While testing out sources for hollow-cathode-exitation several lines in the neon spectrum were discovered. For the most part they have been classified as belonging to already established series.

37. Polarized fluorescence studied by means of a nicol, photocell and amplifier. D. R. MOREY, *Cornell University.* (*Introduced by C. C. Murdock.*)—It becomes a difficult matter to measure the percent of plane polarized light in weak radiations by means of visual devices. This is a serious disadvantage in the study of fluorescence, for polarization measurements yield valuable information on the fluorescent process. A high quality nicol, with ends perpendicular to the length, rigidly fastened to a photoelectric cell may be made to analyze radiations too weak for visual instruments. The types of cell and amplifier to be used are somewhat dependent on the

nature and intensity of the source. Using such an instrument, the effect of inhibitors (KI, KCN, NaBr, etc.) on the polarization of fluorescent bands has been studied. The results strengthen the present view on the nature of fluorescence.

38. Total emissivities at low temperatures and departures from Lambert's cosine law. E. R. BINKLEY, *Lehigh University.* (*Introduced by C. C. Bidwell.*)—Emissivity of oxidized copper, nichrome, brass, cold rolled steel, and of aluminum were measured with a special form of total radiation pyrometer which had a slit opening and linear thermopile, permitting observations at nearly grazing angle. Observations were made at temperatures 100°C, 200°C, 300°C, 400°C, 500°C, on each surface and at each temperature at angles ranging from 0° to 85°. The instrument was calibrated on a camphor blacked surface assumed at 98% black body. Lambert's cosine law is found to hold at angles of observation above 60° but an increasing deviation is found for all surfaces when the angle is reduced below 60°, the deviation at 85° becoming as much as 30% for copper, 39% for rolled steel, 56% for nichrome. The value of normal emissivities for the various surfaces at 500° were as follows: copper 0.74; nichrome 0.95; brass 0.68; cold rolled steel 0.93; aluminum 0.29. There was found to be a rise in emissivity with temperature.

39. Absorption and temperature emission of neodymium in various solvents. R. W. WOOD, *Johns Hopkins University.*—A solid solution of neodymium oxide in fused quartz was drawn out into fibres about 0.3 mm in diameter, and a fiber mounted vertically in a bunsen flame. It glowed brilliantly and when viewed through a direct vision prism exhibited a spectrum consisting of a green, yellow and red band with perfectly dark regions between them. (Experiment shown.) This is undoubtedly the best example of a highly selective temperature radiator ever observed. Seven bands have been photographed between the blue and 0.9μ. An interesting study has been made of solutions of various colored salts in liquid anhydrous ammonia. The rather wide band in the yellow of neodymium ammonium nitrate splits up into five narrow bands. These have been compared with the bands shown by the crystals at liquid air temperature and in solid ammonia. Some results of interest in connection with ray filters have been secured with the ammonia solutions and it seems possible that a suitable filter for giving a comparison spectrum in stellar spectra made with the objective prism may be constructed along these lines. Exhibition of stereoscopic photographs illustrating the orbital motion of the electron in the Stark effect.

40. Paschen-Back effect and hyperfine structure of Bi II. J. B. GREEN, *Ohio State University.* (*John Simon Guggenheim Memorial Fellow, Univ. of Tübingen.*)—The Zeeman effect in Bi II has been studied in a field of 34,000 gausses. The hyperfine structure of Bi II shows some very large separations and the Zeeman patterns yield very interesting results, since the field strengths available give separations that are about midway between "weak" fields and "strong" fields. In particular, λ5719, a $1 \rightarrow 0$ jump in j, gives a completely resolved pattern in the perpendicular polarization, consisting of twenty components, twelve for $m_j = 1$ and eight for $m_j = -1$, thus verifying the nuclear moment of $i = 4\ 1/2$ for Bi. Fisher and Goudsmit's results for the hyperfine structure in Bi II were used.

41. Effect of combined electric and magnetic fields on the helium spectrum II. J. S. FOSTER, *McGill University.*—In electric and magnetic fields crossed at right angles, the diffuse and fundamental series of helium show a fine structure which is sensitive to changes in the electric field. Effects are similar for members of a single series and differ little from the normal Zeeman effect in the sharp and principal series. The splitting has been found to be less than normal in the $p - p$ combination series. A full account of this research will soon appear.

42. The Stark-effect in xenon. H. W. HARKNESS AND J. F. HEARD, *McGill University.* (*Introduced by J. S. Foster.*)—Earlier results with complex spectra have been interpreted to show that displacements of spectral terms by electric fields are inversely proportional to the corresponding hydrogen difference provided the latter are not too small. This view altogether fails to account for the present observation. Instead, a qualitative explanation of most displacements is afforded through the separations of the xenon term from its neighbor in the manner indicated in the approximation made by Pauli. Some of the red lines show more complex patterns than have been found in the other rare gases. In contrast with helium and neon these pat-

terns indicate that the m values are determined as components of the j, which is retained as a unit. For example, the line $2p_3-6d_4^1$ (j:4→3) shows four π components and five σ components, i.e. all that could be observed if the separations in the $2p_3$ state are small.

43. Asymmetry observed in the Stark-components of Hα. D. R. McRae, *McGill University.* (*Introduced by J. S. Foster.*)—A special grating, with a dispersion of 3.8A/mm., having a very intense first order spectrum on one side, has been used to resolve the Stark components of Hα as seen from a Lo Surdo source. An asymmetry is observed in the displacements of the components, which is in general qualitative agreement with the calculations of Schlapp. There are certain discrepancies, however, which have not been explained. An asymmetry in the relative intensities of the components has also been observed. This asymmetry decreases with lower gas pressures, or with increasing propertions of helium, neon, or xenon in the discharge tube, until there is agreement with theory when traces of hydrogen are present in these gases. It may be shown that altering the number of atoms in the initial states does not explain completely the observed asymmetry. Since the probabilities of transition agree with experiment in the cases mentioned it seems that the presence of neighboring hydrogen atoms or molecules may in some way alter the intensities by an action such as collisions of the second kind; but it is difficult to see how this could be carried out in the selective manner required to explain the observations.

44. The electric field, atmosphere and effective temperature of the sun. Ross Gunn, *Naval Research Laboratory, Washington, D.C.*—The study of important electromagnetic effects in the solar atmosphere undertaken in previous papers is continued. It is shown that the large observed spread of effective temperatures of the sun's radiation can be accounted for by the presence of electric and magnetic fields in the solar atmosphere. The magnitude of the electric field at a level where the magnetic field is 25 gauss, calculated from the observed spread of temperatures, is found to be 0.015 volts/cm and agrees well with 0.013 volts/cm calculated earlier from the observed anomalous motions of the solar atmosphere. Gravitational equilibrium is found to be unnecessary in all regions of the atmosphere and it is shown that the "support" and stability of the chromosphere and its anomalous eastward motion are evidences of precisely the same electromagnetic mechanism. An electric field of the value given above is shown to account qualitatively for certain bright line spectra of the sun. The strange observed relation between bright line spectra and rapid axial rotation of stars, just announced by Dr. Struve of the Yerkes Observatory, confirms in a striking manner some of the conclusions of this and earlier papers.

45. Some new relations in the photographic effects of alpha-rays. T. R. Wilkins and R. Wolfe. *Institute of Applied Optics, University of Rochester.*—Jacobsen has recently shown that the number of grains made developable in a photographic plate is proportional to the density provided this number does not exceed 200,000 per sq. mm. The number of developable grains was assumed equal to the number of alpha-particles. In the present work alpha-rays of various speeds have been used with Eastman Slow Lantern plates. For a given exposure time the density is found to be proportional to the number of alpha-rays at least up to 1.5×10^6 per sq. mm determined by a direct scintillation count (density 1.39). It would seem that the lack of linearity in previous work has been due to a variable exposure time. The slopes corresponding to increased exposures are a linear function of the exposure time up to 40 hrs. Thus there is a very marked reciprocity defect in the density amounting to approximately 50% for a 60 hr. exposure. Equations connecting the number of grains per cc of the emulsion with the number of alpha-particles have been obtained. Provided that the reciprocity correction for a given emulsion has been determined, the photographic plate offers a splendid quantitative means for alpha-ray counting.

46. Continuous ultra-γ spectrum explaining cosmic-ray ionization-depth curve data. Charles M. Olmsted, *Buffalo, N.Y.*—It is shown that the ultra-γ cosmic-radiation data published by Millikan and Cameron, (Phys. Rev. **37**, 235 (1931)) may be completely explained by a continuous spectrum of energy falling off suddenly on the short wave side of 0.000013A (as determined by the Klein-Nishina formula; $\mu=0.03$) and extending on the long wave-length side with evenly varying intensity to beyond 0.0008A. Tables of values of intensity of ionization

for different values of μ and λ are given. Tables comparing the computed values of ionization at various depths with the values observed by Millikan and Cameron are given. It is shown that the absorption curve computed from the continuous spectrum coincides with the observed curve as closely as does the curve computed by Millikan and Cameron from a group of four bands having frequencies corresponding to the formation out of hydrogen of helium, oxygen, silicon, and iron. The location of the short wave end of the spectrum at a frequency corresponding to the union of electron and proton, together with the shape of the intensity curve, is discussed from the point of view of astrophysics.

47. Wave packets. D. G. BOURGIN, *University of Illinois.*—(I) The formal character of wave packets follows from the equivalence of harmonic and damped waves in representing disturbances. Real integrals are thus replaced by equivalent complex contour integrals. A true "stationary phase" principle depends on certain "sattel-punkt" contours and is described physically as the resultant of a group of damped harmonic waves of varying amplitudes but identical phases. The "Kelvin stationary phase" principle is misnamed since there, amplitudes, not phases, are constant. Huyghen's principle for odd, non-isotropic negligibly absorptive spaces may be generalized by correlating "paths," extensions of rays, with classes of spatially damped waves. (II) Flamm, Phys. Zeits. Dec. 1928 and others attempt to construct permanent atom packets of the form

$$\psi(x,t) = \sum_{-\infty}^{\infty}\left(\nu_0 \int_0^{1/\nu_0} \psi(0,T)e^{2\pi i n\nu_0 T}dT\right)e^{2\pi i[x/\lambda_n - n\nu_0 t]} \tag{1}$$

with independent λ's (considered atomic characteristic values). This procedure is incorrect for not only is $\int_x \int \psi\bar{\psi}$ infinite but, under some convergence restrictions (1) in its space dependence is an "almost periodic function" i.e. each set of regional values is almost reproduced an infinite number of times contrary to the assumption "nür in einem beshränkten Bereich . . . merklich von Null vershieden."

48. Wave mechanics of electrons in uniform crossed fields. MILTON S. PLESSET, *Yale University.*—We consider the motion of electrons in a uniform magnetic field H in the z-direction and a uniform electric field E in the y-direction. We take for the vector potential $\mathbf{A} = -\mathbf{i}Hy$ and for the scalar potential $V = -Ey$. With these potentials the wave equation does not contain x explicitly, and the solution may be written as $\psi = e^{2\pi i ax/h}\,\Phi_n(u)$ where $\Phi_n(u)$ is the n^{th} orthogonal function of Hermite (the characteristic function for the simple harmonic oscillator);

$$u = (2k)^{1/2}\left[y - \pi/k^2h^2(\pi meE - akh)\right];\ k = \pi eH/hc.$$

The energy is related not only to the values of the fields E and H and to the integral values n, but to the arbitrary constant a as well. The component of the current density in the y-direction vanishes identically; and for the component of the current density in the x-direction we have a function of y alone which is

$$j_x = e^2H/mc\left[\Phi_n(u)\right]^2(y + \pi a/kh).$$

Thus j_x vanishes at the n roots of Φ_n and at $y = -\pi a/kh$; for this latter value the current reverses its direction.

49. Oscillations due to corona discharges on wires. R. E. TARPLEY, J. T. TYKOCINER AND E. B. PAINE, *University of Illinois.*—An experimental arrangement was used in which the electric constants of the circuit containing a corona tube corresponded to much higher frequencies than could be recorded by a reflecting mirror oscillograph. By amplifying the corona currents 300 to 3000 times it was found with this oscillograph, which was insensitive to circuit oscillations, that corona discharges produce a new type of oscillations whose chief characteristics are as follows: The frequency (2000–10,000 cycles) is independent of circuit constants. The amplitude decreases with increasing applied potentials. The wave has a complex form of distinct ripples superimposed upon the charging a.c. or upon the steady part of applied d.c. The wave form depends on the pressure and nature of the gas and on the polarity of the wire. The wave form varies for different gases but the character of the oscillations remains the same for air, CO_2 and N_2. The wave form becomes simpler with decreasing gas pressures especially with

CO_2. At high pressures the oscillations appear superimposed on the corona humps of the charging current at moments when the wire is the cathode, but at lower pressures oscillations appear only when the wire is the anode. No oscillations are obtained with oxidized or corroded wires. Details of the investigation will be published in a bulletin of the Eng. Exp. Station, University of Illinois.

50. Detection and comparative measurement of ionization in dielectrics by means of oscillations. J. T. TYKOCINER AND E. B. PAINE, *University of Illinois.*—In the study of dielectrics subjected to high potentials, minute voids and adsorbed gas bubbles give rise to ionization. The latter causes a redistribution of the electric field with the result that impulses of varying intensity are produced in the adjacent circuit. These impulses are made use of in a method for determining the potential at which ionization sets in and for comparing its intensity at varying applied voltages. If the circuit whichcontains the dielectric is aperiodic and is coupled to an amplifier supplied with a detector and current indicator, the impulses may be separated from the charging a.c. A more sensitive arrangement is obtained by tuning the circuit to a convenient frequency. Impulses in form of damped oscillations are then produced which are entirely free from the a.c. component of the charging source. With four stages of amplification, a thermionic detector and a thermionic voltmeter early stages of ionization in various dielectrics and the dependence of the ionization in various dielectrics on the applied voltage was studied. It was found that oscillations of any chosen frequency (100 to 30,000 k.c.) can be produced in a circuit by corona discharges in condensers, paper cables and rubber insulated conductors and their intensity measured by this method. The complete investigation will be published in a bulletin of the Eng. Exp. Station of the Univ. of Illinois.

51. Some properties of foreign and domestic micas. A. B. LEWIS, E. L. HALL AND F. R. CALDWELL, *Bureau of Standards, Washington, D.C.*—A number of samples of mica, fairly representative of the major sources of the world's supply of mica, have been tested for their dielectric constant, power factor, dielectric strength, and ability to withstand elevated temperatures. Average values are given for the dielectric constant and power factor at radio frequencies, and for the dielectric strength at 60 cycles. The data indicate the deviations from these average values which must be expected in commercial lots of mica. It is shown that stains and inclusions seriously affect the power factor of a sample, but have much less effect on the dielectric strength. Most of the samples were unaffected by exposure to temperatures up to 600°C, but above that temperature only the phlogopites can be said to have successfully withstood the elevated temperatures. On the basis of these data it was not possible to distinguish between micas of like commercial grades obtained from different geographical localities.

52. Cathode sputtering in a commercial application. H. F. FRUTH, *Western Electric Company, Hawthorne Station. (Introduced by O. S. Duffendock.)*—Three sputtering units, each one having six cathodes were designed and operated by one man. These units are used to produce the gold contact surfaces on broadcasting microphone diaphragms. In order to get good continuity, adherance, and uniformity a special method of preparing and cleaning the surface was developed. To produce a uniform quality surface and sputtering rate a bleeder valve to control the vacuum to ± 0.05 mm was developed. Sputtered gold surfaces on duralumin microphone diaphragms proved to be more free from pinholes, blisters and corrosion and gave better service than those made by electrolytic plating. On account of a lighter coat possible the diaphragms can be stretched to a higher natural frequency and show less fatigue.

53. Wave form of pulsating D.C. currents produced by FG-67 thyratrons. WAYNE B. NOTTINGHAM, *Bartol Research Foundation.*—A cathode ray oscillograph has been used to study the wave form in different parts of an "inverter" circuit using two General Electric FG-67 Thyratrons. (For the simple inverter circuit see Fig. 41, Hull, Gen. Elec. Rev. **32**, 398, 1929). With the cathodes heated by independent 60 cycles, A. C. windings an "output" can be taken from the lead between the cathode and the negative terminal of the D. C. plate supply. The current flowing in this lead can be made of the "square-top" type up to a frequency of about 6000 cycles per second. The circuit conditions including the plate potential are critical at the highest frequencies while at 500 to 1000 cycles, it is easy to obtain the desired wave form with a wide range

of current and potential conditions. Under the best conditions the time required for the current to rise from zero to its full value was probably not more than 30 microseconds and a slightly shorter time was required for the current to fall from full value to zero. The exact wave form depends on the inductance, capacity and resistance of the D. C. supply. This system has been developed to heat a filament for the investigation of thermionic emission with low accelerations and retarding fields, but undoubtedly has other possible applications.

54. The starting-time of thyratrons. A. W. HULL AND L. B. SNODDY, *General Electric Company.*—Starting-time is defined as the time between the application of grid or plate voltage, and the attainment of full arc current. This time has been studied by means of high frequency alternating voltage, condenser discharge, and cathode ray oscillograms. The observed times depend upon vapor pressure, and upon anode and grid voltages, and lie between one-tenth (0.1) microsecond and 4 microseconds under practical conditions for all commercial thyratrons. Times of the order of one thousandths (0.001) second, as reported by Nottingham, (Journal Franklin Institute **211**, 271, March 1931) have not been observed.

55. Magnetic induction in a projectile shot into a steady field. L. THOMPSON AND N. RIFFOLT, *Naval Proving Ground, Dahlgren, Va.*—For the solution of the equation of interior ballistics it is essential to define the powder burning and bore dissipation functions appropriate to the system. These can be identified by experimental firing which obtains pressure and displacement of projectile as time distributions. The present experiment measures projectile displacement by use of gun coils, mounted at intervals along the bore. A steady current is established in the coils before the round is fired. As the base of the projectile passes from a coil the transient electromotive forces develop a small change in the primary current, the oscillographic record of the secondary impulse having a form facilitating accurate time evaluation. Absolute position at the instant of current maximum, can be checked for new conditioning by means of external screens times of contact being superposed on the record. The coils are the basis, also, for an empirical method of measuring ejection velocities at high angles of projection, and aboard ship. Magnetic lag measurement for this cycle of short duration, .001 second or less, may be practicable with a coil set external to the gun, utilizing difference between flux values for projectile at rest and in motion and with compensation for eddy current.

56. A method for precise speed control developed in connection with an absolute measurement of resistance. FRANK WENNER AND CHESTER PETERSON, *Bureau of Standards, Washington, D.C.*—Any absolute measurement of resistance inherently involves a measurement of length and of time. In one of the methods on which we are working in the Bureau of Standards time enters as the speed of rotation of a direct-current motor. It is not necessary that the speed over very short periods of time be highly constant, but over periods of about 10 seconds and longer the average speed should be constant and known to within one part in 200,000. On the shaft of the motor there is a 1000-cycle generator whose electromotive force is synchronized with a 1000-cycle electromotive force obtained from a piezoelectric oscillator. Synchronization is secured by rectifying and amplifying the instantaneous sum of the two electromotive forces. The amplifier output current has an average value depending upon the phase angle between the two electrical systems. This current actuates a relay controlling power applied across a heavy inductance in one of the armature leads. As a consequence, the average speed of the motor is constant to the same precision as the oscillator frequency, which is stable to within a few parts in ten million. The method of control requires an oscillation of the speed about the average. This oscillation is of short period and small amplitude.

57. Resistance-temperature law for oxides. J. A. OSTEEN, *Lehigh University.* (*Introduced by C. C. Bidwell.*)—Bidwell showed that the resistance temperature law for certain variable conductors (oxides, etc.) was of the form $\rho = Ae^{Q/RT + aT}$. Plotted in the form $(-1/\rho)(d\rho/dT) = [Q/(RT^2)] - a$ he obtained for Fe_2O_3 straight lines with a break near the recalescence point, the two lines having the same y intercept but different slopes. This law was also followed by metallic germanium. The present paper extends this work to zinc oxide and beryllium oxide. Beryllium oxide yields two straight lines showing a transition at 750°C. Zinc oxide yields two straight lines with a transition in the interval 250°C−500°C. The two zinc oxide lines have different

slopes but the same y intercepts. With successive heatings to 1050°C there occurs continued decreases in the slope of the line for the 500°C – 1000°C range but no change in the y intercept. The line for the range 0°C – 250°C changes on successive heatings to 1050°C and finally stabilizes to a value of slope and intercept which repeats on succeeding runs. On the suggestion that the indicated transformation was due to impurity, new material of special purity prepared by the New Jersey Zinc Company was studied. The behavior of this material was found to agree closely with that of the earlier specimen but gave a more clean cut transformation.

58. High resistances made from metallic oxides. E. R. MANN AND D. R. MOREY, *Cornell Univ.* (*Introduced by C. C. Murdock.*)—The object has been to find a simple and rapid means of making high resistors (10^8 to 10^{12} ohms) of good quality. Resistors are made by mixing metallic oxides in suitable binders of an insulating nature. In all specimens, an ageing process occurs. In certain cases, most of the ageing occurs within a few hours and the resistors show but small and slow changes thereafter. In this there is the advantage of the use of the resistor within a short time after it has been made. A further advantage lies in the extreme ease of making. In the matter of size and ultimate constancy these resistors are not superior to some other types made by more painstaking and laborious methods, yet they will serve excellently for many purposes. A large change with temperature is present in most specimens. They have been tested for deviations from Ohm's law and for small fluctuations under working conditions.

59. A new theorem concerning temperature-compensated millivoltmeters used with shunts for the measurement of current. H. B. BROOKS, *Bureau of Standards, Washington, D. C.*—Millivoltmeters are essentially permanent-magnet moving-coil galvanometers for laboratory or switchboard use. The moving coil is of copper or aluminum wire of high temperature coefficient, hence for a given applied voltage the resulting current and deflection will vary greatly with changing temperature. Millivoltmeters are partly or wholly compensated for temperature by connecting a manganin coil in series with the moving coil. To obtain complete compensation in this way requires, on the average, about 200 millivolts at the millivoltmeter terminals for full-scale deflection. This is undesirably high, and the Swinburne method is therefore used to get complete compensation with about 50 millivolts for full-scale deflection. Either kind of compensated millivoltmeter, used with a shunt for current measurements, is compensated (as an ammeter) only when the resistance of the shunt is small relatively to the resistance of the manganin coil in the millivoltmeter. One maker of high-grade compensated millivoltmeters does not care to supply shunts with a rating of less than 30 times the full-scale current of the millivoltmeter. A simple theorem has been found which applies to either type of compensated millivoltmeter and removes the limitation against low-range shunts.

60. An experimental study of the natural widths of the x-ray lines in the L-series spectrum of uranium. JOHN H. WILLIAMS, *University of California.*—The rocking curves of $UL\alpha_1$ in three different anti-parallel positions of the double x-ray spectrometer give a natural width which is practically independent of the dispersion. The natural widths of $UL\alpha_1$ and $UL\beta_1$ have been observed as a function of voltage and no significant dependence was noted. The half widths at half maximum of twelve lines in the uranium L-series spectrum were studied and the results are:

Line	α_1	α_2	β_1	β_2	β_3	β_4	β_5	β_6	γ_1	γ_2	γ_3	γ_4
$\Delta\lambda$ in X.U.	0.439	0.494	0.299	0.369	0.382	0.726	0.252	0.487	0.242	0.57	0.47	0.233
ΔV in volts	6.56	7.20	7.17	8.04	9.40	16.1	5.94	9.71	7.96	19.7	16.2	8.18

Possible correlations with the electron transitions are suggested and the predominance of nuclear effects are evident from the greater widths of lines involving the elliptical orbit L_I. The large natural widths of the lines excludes the possibility of observing the effects of nuclear spin suggested by Breit. The actual shape of the line $UL\alpha_1$ has been investigated and found to approximate that predicted by the classical theory.

61. The width of soft x-ray lines. WILLIAM V. HOUSTON, *California Institute of Technology.*—The most direct experimental evidence as to the distribution of energy levels in a solid crystal comes from the observations on soft x-ray lines. The work of Söderman and others in

the extreme ultraviolet shows that while spark excitation gives sharp lines, excitation of a solid target by electron bombardment gives very broad lines. The shape of these lines, when proper account is taken of the transition probabilities, gives the distribution of the upper, occupied energy levels of the solid. Although it is difficult to infer the energy level distribution from the observations, because of the unknown transition probabilities, it is easy to determine the line shape to be expected from various models. The simple Pauli-Sommerfeld model of perfectly free electrons, gives the correct order of magnitude for the width of the lines, but does not give a very good approximation to the observed shape. If Bloch's method of starting with the functions of the individual atoms is used, the agreement in both shape and width is rather good. The lines of those elements whose outer shells are incomplete, show the sharp falling off on the short wavelength side which is characteristic of the Fermi statistics.

62. Crystal structure of lithium iodate. F. A. BARTA AND W. H. ZACHARIASEN, *University of Chicago.*—The structure of lithium iodate was determined by using the oscillation and powder methods. Lithium iodate is hexagonal with 2 molecules per unit cell of $a=5{,}469\text{A}\pm0.003\text{A}$, $c=5.155\text{A}\pm0.005\text{A}$. The space group assigned is D_6^6 and the atom positions are: 2Li in $(00\frac{1}{4})$ $(00\frac{3}{4})$, 2I in $(\frac{1}{3}\,\frac{2}{3}\,\frac{1}{4})$ $(\frac{2}{3}\,\frac{1}{3}\,\frac{3}{4})$ and 6O in $(u\,u\,0)$ $(0\,\bar{u}\,0)$ $(\bar{u}\,00)$ $(\bar{u}\,\bar{u}\,\frac{1}{2})$ $(0\,u\,\frac{1}{2})$ $(u\,0\,\frac{1}{2})$ with $u=\frac{1}{3}$. The structure is based on hexagonal closest packing, with the lithium and iodine atoms both lying within oxygen octahedra. The atomic distances are Li $-$O and I $-$O $=2.23$A with lithium octahedra sharing faces with each other, one lithium and one iodine octahedra sharing only edges and two iodine octahedra only corners.

63. The refractive indices of potassium chlorate crystals, and the structure of the ClO_3 group. W. H. ZACHARIASEN, *University of Chicago.*—The method developed by W. L. Bragg (Proc. Roy. Soc. London **105,** 370 and **106,** 346 (1924)) has been used in order to calculate the refractive indices of $KClO_3$ crystals from the atomic arrangement. The Cl^{+5} dipole of the ClO_3 group was given one degree of freedom, along the trigonal axis of the radical. The calculations give agreement with the observed birefringence if the height of the Cl^{+5} dipole above the plane of the oxygens is .99A. X-ray determination gives a displacement of .49A. The scattering power for x-rays depends almost entirely upon the K and L electrons. The x-ray method therefore gives us the position of the Cl^{+7} core, whereas the optical calculations fix the position of the dipole. We must suppose the dipole to be formed by a displacement of the core and the two outer electrons. The observations thus indicate that the two valence electrons of Cl^{+5} are displaced with respect to the core, in a direction away from the oxgyen plane. This result is in agreement with the picture of the ClO_3 group given by the author in different publications. The calculated and observed birefringence and refractive indices are:

	Observed	Calculated
α	1.410	1.420
β	1.517	1.535
γ	1.524	1.535
$[(\beta+\gamma)/2]-\alpha$	0.111	0.115

64. The structure of the NO_2 group. G. E. ZIEGLER, *University of Chicago.*—The structure of $NaNO_2$ was determined in order to test W. H. Zachariasen's prediction (in press, Jour. Am. Chem. Soc.) that the NO_2 group would be angular with 120° between the N $-$O bonds. Powder crystal, rotating crystal, and Laue data were used. The lattice is body-centered, orthorhombic, space-group C2v $-$20, with a unit cell $a=3.55$A, $b=5.56$, $c=5.37$ containing 2 molecules. From visually estimated intensities the positions of the atoms are:

Na	0, u, 0;	$\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}$	$u_{Na}=210°$
N	0, u, 0;	$\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}$	$u_N=30°$
O	0, 0, u;	0, 0, $-u$; $\frac{1}{2}$, $\frac{1}{2}$, $u+\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}-u$	$u_0=70°$

(360° = a, b, or c respectively)

Distances between atoms: $N-O=1.13$A, O $-$O same group $=2.09$, O $-$O different groups >3.3, Na $-$O two O's 2.53, Na $-$O four O's $=2.46$. h = displacement of N from O $-$O line $=0.46$ A. The angle between the N $-$O bonds $=130°$. The observed data definitely disagree with a colinear NO_2 group.

65. Precision wave-length measurement with the double crystal x-ray spectrometer. ARTHUR H. COMPTON, *University of Chicago.*—An x-ray spectrometer was designed with the first crystal mounted on an auxiliary table supported by the frame of the spectrometer, and with the second crystal mounted on the central table of the instrument, whose position is read from a precision circle. The ionization chamber (of 25 cc capacity, filled with krypton) is on an arm whose position is read by a second precision circle. The instrument was built by the Societe Genevoise de Physique. The first crystal was adjusted to throw the $K\alpha_1$ line of molybdenum over the main axis of the spectrometer, and measurements were made with the second crystal in the (1, −1), (1, +1), (1, −4) and (1, +4) positions (Allison's notation). The reflection maxima from calcite (corrected to 18°C) occur at $\theta_1 = 6°42'35.5''$ and $\theta_4 = 27°51'32.9''$ with a probable error of 0.25″ due chiefly to errors in reading the circle. Using an apparent grating space for the first order of 3.02904A at 18°C, we get $\lambda = 707.832 \pm 0.002$ mA. Larsson obtained 707.831 ±0.003 mA using Siegbahn's photographic method. Comparison of θ_1 and θ_4 gives for the index of refraction in calcite, $1-\mu = (2.10 \pm 0.15) \times 10^{-6}$, in good accord with Hatley's more direct measurement of 2.04×10^{-6}.

66. Absolute wave-lengths of the copper and chromium K series. J. A. BEARDEN, *Johns Hopkins University.*—A consideration of the objections to the measurement of x-ray wave-lengths by ruled gratings shows that the method should be reliable if the apparatus is in precise adjustment and the gratings of good quality. In the present experiments 5 gratings were used which were ruled on two ruling engines. The method of the experiment was similar to that given by the writer in the Proc. of the Nat. Acad. of Sci. **15,** 528, (1929). The results from different gratings on the same wave-length agree very satisfactorily. The final results of 172 plates are given in the following table.

Spectral Line	Crystal λ	Grating λ	Limiting Error	Grating λ −Crystal λ
Cu K_β	1.38914A	1.39225A	±0.00014A	+0.224%
Cu K_α	1.53838	1.54172	± .00015	+ .217
Cr K_β	2.08017	2.08478	± .00021	± .222
Cr K_α	2.28590	2.29097	± .00023	+ .222

From these results, the grating constant of calcite is $d = 3.0359 \pm 0.0003$A, and Planck's constant h as determined by Duane, Palmer and Yeh is $h = 6.573 \pm 0.007 \times 10^{-27}$ erg sec. The mean value of the dispersion of x-rays as determined by Stauss (Phys. Rev. **36,** 1101, (1930)) and Larsson (Inaugural Dissertation, Uppsala, 1929) gives $e/m = 1.769 \times 10^7$ e.m.u. g^{-1}. The values of these constants are independent of any imperfection in the crystal grating. If the crystal lattice is assumed "perfect" then we have, Avogadro's number $N = 6.019 \times 10^{23}$ mol. per mol. the charge on the electron $e = 4.806 \times 10^{-13}$ e.s.u. and $h = 6.623 \times 10^{-27}$ erg. sec.

67. Absolute measurement of the Cu L_α line. CARL E. HOWE AND MILDRED ALLEN, *Oberlin College.*—Two photographic plates at different distances from a plane glass grating of 600 lines/mm are exposed simultaneously to the radiation from a copper target. Wave-lengths are computed from the plates and the constants of the apparatus. Over sixty determinations indicate for the wave-length of the L_α line of copper a value close to 13.326A ±0.01 (mean deviation) ±0.001 (probable error). This differs by 0.15% from 13.306A as obtained by Larsson from crystal measurements.

68. Theory of the diffuse scattering of x-rays by solids. G. E. M. JAUNCEY, *Washington University, St. Louis.*—The classical theory of x-ray scattering has been applied to the scattering of x-rays by the electrons in the atoms of a solid. The case in which the solid consists of atoms of one kind has been considered. The interaction of the waves scattered by each electron with these scattered by every other electron in the solid has been considered. The analysis is simplified by the fact that the orbital periods of the electrons in the atoms are very much shorter than the vibrational periods of the atoms, due to thermal agitation. The final formula obtained is $S = 1 + (Z-1)(f'^2/Z^2) + (F^2/ZN)X$ where S is the scattered intensity per electron relative to the scattered intensity from a single isolated electron, Z is the atomic number, F the atomic struc-

ture factor including the effect of thermal agitation f' is related to f the true atomic structure factor (without thermal agitation), N is the total number of atoms, and X is a certain double summation. The value of X has not been obtained for an amorphous substance, but it has been evaluated for the case of a simple cubic crystal by Jauncey and Harvey in another paper (No. 153).

69. Hyperfine structure and width of x-ray spectral lines. F. K. RICHTMYER AND S. W. BARNES, *Cornell University.*—In a recent letter to the Physical Review (Sept., 1930) we reported measurements which seemed to indicate that the $K\alpha_1$ line of W(79) has a hyperfine structure of the type predicted by Breit. The measurements were made with a two-crystal spectrometer of special design. It now appears, after further critical and extensive study, that the apparent separation must have been due to some (as yet) unknown instrumental peculiarity. The numerous measurements made in connection with this study permit a determination of the width of $WK\alpha_1$. The average of several measurements in second, third and fourth order, after applying corrections for rocking curves of the crystals in the parallel position, gives a half width of 0.154 X.U.

70. Survey of the satellites of the $K\alpha_{1,2}$ doublet, the $K\beta_1$ and $K\beta_2$ lines. O. REX FORD, *West Virginia University. (Introduced by R. C. Colwell.)*—In a paper on the satellite structure of the x-ray diagram lines $L\alpha_1$ $L\beta_1$ and $L\beta_2$ for the elements Rb (37) to Sn (50) Richtmyer and Richtmyer, by a careful timing of exposures, were able to show that the number of satellites were more numerous than previously reported. These results called for a survey of the satellite structure of the K-diagram lines. Such a survey extended the range of the elements over which the satellites $K\alpha_3$, $K\alpha_4$ and $K\alpha'$ could be measured. An entirely new satellite of the diagram line $K\beta_1$, designated by $K\beta^\circ$, was found for the elements Ca(20) to Cr(24). The satellite $K\alpha_3$ was found to consist of two components over the range of elements Al(13) to Cl(17) instead of a singlet as previously supposed. Microphotometer records of the spectrograms show a very significant reversal in the relative intensities of the $K\alpha_3$ and $K\alpha_4$ satellites at the element P(15). That the square root of the difference in frequency between a satellite and its parent line is a linear function of the atomic number is shown to be approximately true for satellites of the $K\alpha_{1,2}$ doublet. This relation is not valid for satellites of $K\beta_1$ and $K\beta_2$.

71. Effect of piezoelectric oscillations on the Laue patterns of quartz. G. W. FOX AND P. H. CARR, *Iowa State College.*—In an attempt to determine the amplitude of vibration of the atoms in a quartz lattice brought about by piezoelectric oscillations, a series of Laue photographs have been made of both Curie and thirty-degree cut plates, using the white radiation from a standard Coolidge tube. This tube had a tungsten anode and carried a current of four milliamperes at 95 kilovolts. Eastman standard x-ray film was used with no sensitizing screens. On examination, the patterns produced by each plate, oscillating and non-oscillating, appear identical except in one respect: the pattern of the oscillating plate is several times as intense as that of the non-oscillating. A four-hour exposure of a non-oscillating plate to radiation of the above mentioned type, produces but the rudiments of a pattern, whereas, the same plate oscillating produces a very beautiful intense pattern for the same time of exposure. The effect is quite independent of the piezoelectric frequency and does not depend on whether the plate vibrates according to the shear mode or the transverse mode. It is hoped that the work in progress will establish the cause of this peculiar intensity difference.

72. Calculation of the resolving power attainable in x-ray spectroscopy by photographic methods. SAMUEL K. ALLISON, *University of Chicago.*—If w_c, the (half) range of glancing angle over which a crystal will reflect monochromatic x-rays has been determined by the double spectrometer method, it is possible to calculate what resolving power is attainable from this crystal by photographic methods. Equations are set up giving the resolving power in terms of a, the slit width, and R, the distance from slit to photographic plate. Some results are: (1) No appreciable increase in resolving power is obtained by making $a/2R < \frac{1}{4}w_c$. (2) If $a/2R > 2.5w_c$ the resolving power does not involve w_c. (3) The resolving power attainable in the first order by photographic methods is $1/2^{1/2}$ of that attained in a double spectrometer in the (1, 1) position with crystals of equal perfection, as stated by Valasek (Phys. Rev. **36,** 1523 (1930).) (4) The

resolving power of the instrument used by Valasek in his experiments on the molybdenum K spectrum in the first order was about 5350, whereas that of a double spectrometer in the (1, 1) position with crystals of the perfection of those used by Allison and Williams (Phys. Rev. **35,** 1476 (1930)) is about 8100. The calculations are extended to include measurements of widths of spectrum lines by photographic methods.

73. Indices of refraction and absorption in the case of soft x-rays. ELMER DERSHEM, *University of Chicago.*—Measurements of the absorption of the $K\alpha$ line of carbon in carbon, nitrogen, oxygen and neon indicate that for elements such that $\lambda_K < 44.6\text{A} < \lambda_{L_I}$ the atomic absorption coefficient is given by the following equation: $\mu_a = 1.65Z^{4.4} \times 10^{-23}$. The linear absorption coefficient of fused quartz may be calculated from its density and the absorption coefficients of its constituents and is found to be 47,200. The index of absorption κ, is found from the equation $\kappa = \mu\lambda/4\pi = 1.68 \times 10^{-3}$. The Drude-Lorentz dispersion formula yields the value, $\delta = 1 - n = 4.8 \times 10^{-3}$. Reflected intensities computed from these values are somewhat higher than those found experimentally. Good agreement is secured if κ is assumed to be 2.5×10^{-3}. The results indicate that the value of δ computed from the Drude-Lorentz formula is the correct one but that surface films or imperfections reduce the reflected intensity in much the same manner as an increase of absorption. Other measured values of atomic absorption coefficients for the $K\alpha$ line of carbon are as follows: A, 30.1×10^{-19}: Kr, 43.4×10^{-19}: Xe, 14.5×10^{-19}: Au, 40.7×10^{-19}. The bearing of these results upon x-ray absorption formulas is discussed.

74. Change in x-ray wave-lengths by partial absorption. J. M. CORK, *University of Michigan.*—Experiments have been carried out to duplicate those of Dr. B. B. Ray, in which a beam of x-rays traversing an absorbing medium gave in the direction of transmission a modified line of longer wave-length. The shift in wave-length corresponded to the x-ray photon elevating an electron to an outer atomic level and passing on unchanged in direction with diminished energy and hence a longer wave-length. Using the $K\alpha$ lines of copper and the $L\alpha$ line of tungsten with absorbing screens of beryllium, boron, carbon, oxygen and nitrogen under a variety of conditions, it has been impossible to show the existence, in any case, of a modified line.

75. X-ray absorption measurements in mercury vapor. FRED M. UBER, *University of California.* (*Introduced by Robert B. Brode.*)—The mass absorption coefficients, μ/ρ, of mercury in the wave-length region 0.74 to 1.4A were determined by an ionization method. The absorber was in the form of superheated vapor, whose density was calculated on the assumption of perfect gas behavior. The absorption chamber was entirely of pyrex glass, and was combined with the x-ray tube into a single unit. Electrometer deflections of several millimeters per second were obtained with the tube currents ranging from 6.5 to 17.5 m.a. and with the voltage low enough to prevent excitation of wave-lengths corresponding to the second order reflection. Readings were taken for several positions of the crystal before removing the absorbing vapor from the path of the beam. The magnitudes, δ, of the three L absorption discontinuities, where δ is defined as the ratio of μ/ρ on the short and long wave-length sides of the limit, are $\delta L_I = 1.18$, $\delta L_{II} = 1.39$, $\delta L_{III} = 2.45$. The mass absorption coefficient can be expressed by the relation $\mu/\rho = A\lambda^c$. The constant A assumes a different value for each branch of the curve, but the value of c does not vary from 2.6 by more than 0.1 for all four branches. The value of μ/ρ at 1.4A is in accord with what one would expect from Allen's values for gold and lead, which indicates that no appreciable error is introduced by using the perfect gas equation for superheated mercury vapor.

76. Lattice parameter of copper by a precision instrument. C. S. BARRETT AND H. F. KAISER, *Naval Research Laboratory, Washington, D. C.*—A precision x-ray camera for large angle diffraction, a modification of the instrument of Sachs (Phys. Zeit. **60,** 481, 1930), has been constructed. A photographic plate is used, avoiding film shrinkage. A specimen is used whose surface is plane, parallel to the photographic plate, and perpendicular to the x-ray beam. The distance from specimen to plate is measured by a micrometer. The instrument is applicable to specimens prepared for metallographic examination, and is convenient for high temperature studies. The parameter of copper was determined for material from Adam Hilger Ltd. analyzing

Oxygen 0.040%, Nickel 0.002%, Iron 0.003%, Arsenic 0.004%, Lead 0.001%, Calcium 0.001%, with spectroscopic analysis indicating in addition only slight traces of magnesium, caesium, and sodium. The specimen was prepared with a polished surface, annealed two hours in vacuum, and etched lightly. Copper and brass anticathodes were used. Wave-lengths assumed were Cu $K\alpha_1 = 1.53739$A, Cu $K\alpha_2 = 1.54126$A, Zn $K\alpha_1 = 1.43206$A, Zn $K\alpha_2 = 1.43587$A. The mean value of 18 observations of a_0 for copper at 20°C was 3.6078 ± 0.0001. This value agrees closely with that of Ageew, Hansen, and Sachs, (Phys. Zeit. **66,** 350, 1930), 3.6081A and yields a calculated density of 8.93 in accord with measured densities, 8.94 ± 0.01 (I.C.T. Vol. II, p. 456).

77 Lattice parameters of solid solutions of silicon in copper. H. F. KAISER AND C. S. BARRETT, *Naval Research Laboratory, Washington, D. C.*—Measurements of a_0 for α-Cu-Si alloys containing less than 0.06% total impurities were made on the precision instrument described above. The alloys were homogenized by a 48 hour anneal at 750°C in vacuum, terminated by a quench in water. After a polish, they were given a 3 hour anneal at 725°C in purified hydrogen and again quenched in water. Subsequent polishing and etching was done with great care to provide a surface free from cold work, and exposures were made within 24 hours; these precautions were taken to avoid decomposition of the solid solutions. Alloys containing 5.91% and 6.36% Si, however, showed by their diffraction patterns and by their a_0 values that there was precipitate present. The parameters found were as follows in A.U. at 20°C: 1.09% Si = 3.6103; 3.01% Si = 3.6128; 5.02% Si = 3.6150; 5.91% Si = 3.6151; 6.36% Si = 3.6157. Densities calculated from these parameters and compared with densities as measured by Norbury (Trans. Farad Soc. **19,** 586, 1923–24) indicate that the solid solution is of the simple substitutional type, and agree well with Norbury's densities when calculated on this theory. That the silicon atom expands the copper lattice in spite of its smaller radius is not regarded as an anomaly, since the elements differ in crystal structure. Studies of orientation of the precipitate are being conducted.

78. The x-ray analysis of vesuvianite. B. E. WARREN, *Massachusetts Institute of Technology.*—Vesuvianite $H_2Ca_{10}Al_6Si_9O_{38}$ is a complex, tetragonal silicate with $a = 15.60$A $c = 11.83$A space group D_{4h}^{4} and four molecules in the unit cell. The cell contains 260 atoms and involves 44 parameters. The analysis is of particular interest as an extreme case of a complex structure, and illustrates the extent to which our present knowledge of the physical chemistry of the silicates has progressed. The structure is determined by means of a close relationship which is discovered between vesuvianite and the cubic crystal garnet $Ca_3Al_2Si_3O_{12}$. Two quadrants in the vesuvianite unit cell are identical in structure to the corresponding two quadrants in garnet except that they are rotated 45° about c. Quantitative measurements of the integrated reflexion with a Bragg ionization spectrometer for 40 planes give structure amplitudes in good agreement with those calculated from the structure. The structure contains SiO_4 and Si_2O_7 groups, and the coordination numbers are Si-4, Al-6, Ca-8.

79. Atomic scattering power of copper and oxygen in cuprous oxide. G. A. MORTON, *Massachusetts Institute of Technology. Rockefeller Institute for Medical Research. (Introduced by B. E. Warren.)*—The atomic F-curves for copper and oxygen for the $K\alpha$ radiation of copper have been determined from cuprous oxide, and are compared with the F_{Cu}-curve from metallic copper and F_O-curve from NiO. Measurements were made on samples of finely powdered Cu_2O pressed into suitable briquets, using an x-ray powder spectrometer to measure reflected intensity. The structure factor F for the reflecting planes is calculated from the power of reflexion. The atomic scattering factors as a function of $\sin\theta/\lambda$ are found from these F values. The F_{Cu}-curve and F_O-curve as obtained from Cu_2O and those from metallic copper and oxygen in NiO are found to be the same over the overlapping portions of the curves.

80. An x-ray determination of crystal orientation in nickel, copper and aluminum, produced by cold rolling. C. B. HOLLABAUGH AND W. P. DAVEY, *The Pennsylvania State College.*—High purity nickel, copper and aluminum, free from all preferred orientation, were cold rolled in such a way as to produce no appreciable temperature rise and the orientations were determined after each pass using the method of Davey, Nitchie and Fuller (Mines and Met.

Tech. Pub., 243, E88). Nickel and copper showed identical orientations both as to limits of ranges of preferred orientations and mean positions. The number of passes through the rolls determines the probability that a crystal fragment will be within the preferred range, but does not affect the limits of the preferred range. Aluminum shows a related preferred orientation, but with widely different angular limits which depend on the number of passes through the rolls. This work, with similar work on silver previously reported, shows, contrary to the accepted belief, that except for copper and nickel, the common face-centered cubic metals show differences in preferred orientation both with respect to the limits of preferred range and with respect to the mean position of orientation. The preferred positions are similar only in that they all show one face diagonal of the cube always in a plane parallel to the direction of rolling and perpendicular to the rolling surface.

81. X-ray evidence as to the size of a gene. OSWALD BLACKWOOD, *University of Pittsburgh.*—To explain certain facts of heredity, geneticists postulate the existence of bodies called genes in the chromosomes of living cells. The diameter of these bodies in the cells of the fruit fly (Drosophila) is roughly estimated to be 600A. The writer has computed the approximate number of ions produced in such a gene when exposed to x-rays of known intensity for a known time. Using Patterson's experimental value for the percentage of exposed flies showing a certain mutation about one per cent of the atoms in a gene are found to be "sensitive," (i.e. their ionization is assumed to be accompanied by mutation). If the sensitive material were concentrated in a spherical nucleus, its diameter would be about one-fifth that of the gene. The hypothesis that natural mutations are caused by cosmic or natural gamma-rays seems improbable since the ionization produced in this manner is about three billion times smaller than that due to the x-rays as used by Patterson. The period for one per cent mutation would therefore be about one million years instead of a few weeks.

82. Parallax stereoscopic x-ray pictures. KENNETH S. COLE, *Columbia University.*—Shadow parallax "stereograms" and "panoramagrams" can be made with visible light or x-rays by several types of relative motion of a point source of radiation, the object, a suitable grating, and the photographic plate. Viewed with a similar grating, either a stereoscopic or pseudoscopic effect may be obtained, also, small movements of the object can be followed in the "panoramagram." Stereoscopic x-ray "vision" can be obtained with a fluorescent screen and two gratings.

83. The lethal effect of intense x-rays on the organism colpidium colpoda. HARRY CLARK, MORDEN BROWN, AND JOHN THOMAS, *Stanford University.*—Several single-cell organisms have been studied by various investigators. The curves showing the relation between the number of survivors of a group and the time of radiation have been fitted usually by the use of Poisson's exponential series, the number of terms required lying between 1 and 8 with one exception. The results are generally interpreted as statistical evidence of a definite lethal number of quantum-hits, which must fall inside a small "sensitive volume" within the cell, although normal biological variation is sometimes considered. Although Crowther, working with colpidium colpoda, used 49 terms for immediate death, the range of individual lethal doses was still very wide. Using silver radiation at 50 kv, several times more intense than Crowther's and well controlled, we have found evidence of an approach to a critical lethal dose, the same for all individuals, which would exclude normal biological variation. To reconcile this result with Crowther's, we suggest that the processes to recuperation, which are known to be very rapid, are less rapid in the sensitive volume than elsewhere. Less intense radiation produces death by injury to the sensitive volume; more intense rays operate predominantly on other parts of the cell.

84. The extension of Clapeyron-Clausius equation to dissociation within the gaseous phase. J. L. FINCK, *Washington, D. C.*—This paper is a study of the thermodynamic analogies between the liquid-vapor state and the gaseous state in which dissociation occurs. It is noted that the associated gaseous component corresponds to the saturated liquid and that the dissociated gaseous component is the analogue to the saturated vapor. By means of a hypothetical

mechanism, consisting of a piston and cylinder, which contains the gas, and two semi-permeable membranes, it is possible to separate the gas into two phases, one containing the associated component and the second the dissociated component. This permits dissociation to take place by an isothermal-isopiestic process, analogous to the evaporation of a liquid. By means of this hypothetical process it is shown that Clapeyron-Clausius equation must take the form $\Lambda = \theta(v_2 - v_1)(\delta p/\delta\theta)_x$, where Λ is the heat of dissociation, v_1 and v_2 the specific volumes of the associated and dissociated components, each taken at p, θ, and x is the degree of dissociation. Calculations based on experimental data for NH_3, H_2O, and CO_2 gases check the experimentally determined values for Λ to 1 percent and less. Some remarks are made with regard to superheated and supercooled states.

85. The mechanics of effervescence. C. J. CRAVEN AND OTTO STUHLMAN, JR., *University of North Carolina.*—Small bubbles of gas rising through a liquid originating at various depths, great compared to their dimensions, arrive along a spiral path, at the surface with the same terminal velocity. They roll under the surface film, come to rest and burst, projecting fragments of liquid into the air. These fragments rise to different heights. For a given radius of bubble, temperature remaining constant, the separate fragments follow a near Maxwellian distribution when distribution in height is examined as a function of diameter of bubble. After the maximum height is passed the above distribution becomes less regular, probably due to distortion in shape of the larger bubbles. Bubbles rising through water at 21°C, having diameters up to 0.16 cm burst into three fragments, from 0.16 to 0.20 cm they burst into two fragments. Bubbles larger than this burst irregularly.

86. The absorption of audible vibrations in the air. VERN O. KNUDSEN AND L. P. DELSASSO, *University of California at Los Angeles.*—Recent measurements on the absorption of high pitched sound in air show (1) that the absorption is several times greater than that accounted for by viscosity, heat conduction and radiation losses, and (2) that the absorption decreases as the amount of water vapor in the air increases. By making reverberation measurements in two rooms which have the same boundary material (painted concrete) but different "mean free paths," it is possible to eliminate the surface absorption, and thus determine the absorption in the air only. Measurements obtained to date, both in the two room experiments and in the free atmosphere, indicate that at a frequency of 4096 cycles, for example, the attenuation constant at 21°C and 20% relative humidity is about 0.00009 and at 70% relative humidity is about 0.00005 C.G.S. units. In a mixture of air and CO_2 (4% by volume) there was evidence of a slight increase in absorption owing to the presence of CO_2. The data have a bearing upon problems in sound signaling and in architectural acoustics, and may have a bearing upon the absorption of energy within the molecule.

87. The flow of gases through porous materials. H. G. BOTSET AND M. MUSKAT, *Gulf Research Laboratory, Pittsburgh, Pa.*—An experimental study has been made to establish quantitatively the characteristics of and laws governing the flow of gases through consolidated and unconsolidated porous materials of fine texture. Experiments were performed with columns of glass beads, homogeneous and heterogeneous unconsolidated sands, as well as with samples of actual sandstones. With the sandstones linear flows were made both perpendicular and parallel to the bedding plane. Radial flows through annular sections of the sandstone were also made. In all cases it was found that the gradient of the squares of the pressures is proportional to a power of the mass velocity. In the various cases the exponent was found to lie between the limits 1 and 2 corresponding respectively to completely viscous and completely turbulent flow in straight cylindrical tubes. For a given sand however it remains fairly constant over a considerable range in the mass velocity. On the basis of these results a theory was developed for the production from and pressure decline in a closed sand reservoir of uniform thickness producing into a well under conditions of radial two-dimensional flow. The theoretical predictions check qualitatively with the limited field data that are available.

88. Molecular flow and the formation of beams. A. ELLETT, *State University of Iowa.*—The streaming of air at low pressure through short circular tubes is shown to give rise to an angular distribution of the molecules emerging from the tube in fair agreement with the cal-

culations of P. Clausing (Zeits. f. Physik **66,** 471, 1930). Measurements were made by means of a Pirani gauge.

89. The Brownian motion of strings and elastic rods. G. A. VAN LEAR, JR., AND G. E. UHLENBECK, *University of Michigan.*—The method introduced by Ornstein is applied to calculate the Brownian-motion mean-square deviation for strings and for elastic rods, the surrounding medium being a gas. For the string, a varying tension and elastic binding at the ends are supposed, and a formula is obtained for the mean-square deviation of any point at time t, having started with a given deviation of that point; the result contains infinite series. This result is specialized to: (1) the string with fixed ends and constant tension, and (2) the string hanging under gravity. In case (1), for the mid-point, and for a limited time interval, the series are summed; for $t\rightarrow\infty$, the result is given for all points, agreeing with that given by Ornstein for the mid-point. Elastic rods are treated similarly, and similar results are obtained. The effect of gravity, when the rod is vertical, is introduced by a simple and consequent perturbation method, and a formula is obtained for the mean-square deviation of the lower end; this agrees closely with Houdijk's experimental results. The time dependence given by the complete formula cannot yet be tested, for Houdijk gives only limiting values in his publication.

90. Pirani gauge applied to the measurement of small pressure changes. R. M. ZABEL AND A. ELLETT, *State University of Iowa.*—The application of the Pirani gauge to the measurement of small pressure changes is discussed. Both nickel and tungsten wires are used as filaments in the gauge. Nickel wire not only has the greater sensitivity but possesses several other advantages. The theory of the gauge is developed so that it is possible to predict the affect of change in length or diameter of the gauge wire upon the sensitivity of the gauge. To obtain maximum sensitivity the wire should be made as long as convenient and its diameter adjusted so that its resistance is approximately equal to the resistance of the galvanometer. Both theory and experiment indicate that the sensitivity of the gauge is increased by increasing the area of the wire or by decreasing the temperature of the walls of the gauge. The theory also predicts that there is an optimum temperature to which the wire should be heated for maximum sensitivity of the gauge. The observed and computed values of the optimum temperature are compared. The maximum sensitivity attained is a galvanometer deflection of 1 mm for a pressure change of air equivalent to $5\pm1\times10^{-9}$mm of mercury.

91. Application of transient network theory to gas flow in vacuum systems. DONALD S. BOND, *University of Chicago.* (*Introduced by Harvey B. Lemon.*)—With complex vacuum systems employing connecting tubing of only moderate diameter, the instantaneous pressure at any point may be calculated with considerable simplicity by employing the electrical analogy. Resistance is defined (by Knudsen's equation) in terms of tube dimensions; capacity (both lumped and distributed), in terms of volume. The network which simulates the most general type of closed vacuum system consists of n T-mesh circuits with resistance and capacity only. The solution of the n mesh equations gives the potential drop (or pressure) across each capacity of the form $e_j=\Sigma a_{jk}\exp(-b_k t)$. The solution can be carried out numerically for any number of meshes. Using curves of this form, which check with experiment at low pressures, it has been possible to correct McLeod and ionization manometer readings to give true pressures at any part of the system. These have been used in the evaluation of true pump speeds. The agreement has given a check on the region over which Knudsen's low-pressure equation is valid.

92. Time-pressure characteristics of some diffusion and molecular pumps. PETER J. MILLS, *University of Chicago.* (*Introduced by Harvey B. Lemon.*)—Observations on various pumps were made of the time rate of change of pressure during the evacuation of a 4 liter volume and of the equilibrium pressure reached when this same 4 liter volume was leaking at a measured rate. The high vacuum pumps included single and multistage, air and water cooled, glass and steel diffusion pumps; and molecular pumps. Most of the diffusion pumps were mercury filled but several were tested with a filling of oils of low vapor pressure. Various backing pressures were obtained from several types of force pumps. Pressures, read on a pair of McLeod gauges and on an ionization manometer, gave apparent speeds from which true pump speeds were calculated by the method outlined in the preceding abstract.

93. The theoretical pressure distribution on wing sections. THEODORE THEODORSEN, *National Advisory Committee for Aeronautics, Langley Field, Virginia.* (*Introduced by J. S. Ames.*)—This paper presents a simple and exact method of calculating the lift distribution on thin wing sections. The angle at which the flow enters the leading edge smoothly is shown to play an important rôle in the theory, and is termed the ideal angle of attack. The lift distribution at this particular angle, termed the "basic distribution," is shown to be a characteristic property of the section. It is shown that the lift of a wing section may be considered to consist of (a) the basic distribution and (b) the additional distribution, the latter being identical for all sections. It is further shown that the additional lift intensity in potential flow of a noncompressible liquid is infinite at the leading edge, and the conclusion is made that the present theory of thin wing sections is applicable only at the ideal angle of attack. The theory is adapted to describe some of the properties of the actual or thick wing sections, and it is established that the essential parameter occurring in this analysis is the radius of curvature at the leading edge. The approximate magnitude and location of the maximum lift intensity is determined.

94. The effect of the presence of a grid upon certain characteristics of the airflow at the surface of an airfoil. MERIT SCOTT, *Cornell University.*—In a previous paper it was reported that the heat dissipation per unit area from the surface of an airfoil, as measured by resistance strips mounted parallel to the span and flush with the surface, is a characteristic of the airflow. An integral relation was set up from which it was shown that the coefficient of heat dissipation is proportional to the velocity gradient at the surface of the airfoil and hence to the viscous resistance. The effect of the presence of a grid, whose position with respect to the airfoil is varied, upon the above mentioned characteristics, has now been observed. It is found that systematic changes in these quantities may be followed as various parameters in the problem are altered. Mathematical treatment appears to be too involved for the present; but qualitative explanation is being attempted in terms of types of flow, the Prantl boundary layer, the Rayleigh surface of separation, etc.

95. Some examples of dimensional analysis. JAKOB KUNZ, *University of Illinois.*—The dimensional analysis has been applied to the following cases. (1) A solid body moves in a viscous medium, so that the motion is essentially determined by the viscosity, a characteristic length of the body, and the velocity, but independent of inertia, i.e., the density. The analysis leads to the formula $F=R\mu vC$. Stokes analysis gives $C=6\pi$. For higher velocity we assume that the viscosity has very little influence and that on the contrary the forces are determined by vortices and waves mixed up, or on the density ρ. The analysis leads to $F=v^2\rho l^2C$, Jonkowski-Cutta found $F=v^2\rho A \sin\alpha\cdot k$ for the lift of an airplane. (2) When the velocity of a projectile approaches that of sound, then the force depends probably on the compressibility of the medium. The force of resistance appears in the form $F=pl^2(v/c)^nC_1$, where c is the velocity of sound. (3) In an analogous way we proceed to study the motion of a fluid in a tube under a pressure gradient P. For a slow laminar motion under the influence of viscosity μ we obtain $P=(v/r^2)\mu C$, which is Poiseuille's law. In the case of turbulent motion we obtain $P=v^2r^{-1}\rho C$, where C is a dimensionless constant. Finally if the velocity is very large, approaching that of sound, P appears in the form: $P=p/r(v/c)^nC$.

96. The Auger effect in atomic spectra. A. G. SHENSTONE, *Princeton University.*—In most complex spectra there are two distinct series limits, the corresponding ions being of different structure. A term built on the ion of higher energy may be above the lower of the two limits. It is then possible for the atom to dissociate spontaneously into an ion plus an electron if there is a correct relationship between the qauntum numbers of the term and those of the ion and electron. The transition probabilities may be expected to be governed by rules similar to those which are applicable in predissociation of molecules. The effect is shown in the terms from the structure d^9s,s in CUI. The terms are ^4D, ^2D, ^2D and the lines due to all the components with $J=1\frac{1}{2}$ or $2\frac{1}{2}$ are absent or extremely weak in low-pressure sources, and very diffuse under high pressure. The ionization transition must be to the ion d^{10} plus a d-electron. The fact that the coupling is not completely Russell-Saunders accounts for the presence of the effect in ^4D. The structure d^9s, d also shows the same type of effect, but the observations are as yet incomplete. In BeI, the lines due to the negative term $3s2p^3P$ are absent in the spectrum

from the Schuler tube but present in high-pressure sources. The negative terms of CaI should show the effect but there are no observations in proper sources.

97. Intensity relations in complex spectra. GEORGE R. HARRISON AND M. H. JOHNSON, JR., *Massachusetts Institute of Technology, and Harvard University.*—A correlation is found between anomalous intensities in multiplets and the presence of neighboring states having the same J values as the perturbed terms. This indicates that the extension of the sum rules ordinarily assumed, in which all lines arising from a given state are summed, is incorrect, and that all similar terms having identical J values and lying near one another must be summed together. A general quantum-mechanical proof has been found that the following rule holds: The relative total intensity of all lines arising from transitions between all states J_1 and J_2 in two configurations is constant for any coupling. Where several configurations overlap the rule must be extended to include the new terms of similar J. Where relatively small departures from LS coupling exist only close-lying terms of similar J need be grouped together. Experimental verification is difficult as generally a large number of lines must be summed, but fragments often serve to test the rule. Confirmatory intensity measurements are presented which prove the interdependence of neighboring terms of common J, and it is shown that intensity anomalies are more sensitive indicators of departures from LS coupling than are the other anomalies associated with it.

98. Electrostatic interactions in (jj) coupling. D. R. INGLIS, *University of Michigan.*—A method is developed for calculating the energy of electrostatic electronic interaction for the various states of an atom in (jj) coupling. The largest perturbation of spin-orbit interaction is first taken into account by using single-electron wave functions stabilized for this interaction. Antisymmetric combinations of products of these form the fundamental wave functions in the perturbation calculation of the electrostatic interaction. The energy is expressed in terms of the same integrals that Slater (Phys. Rev. **34,** (1293)) met in the case of (LS) coupling, and one new integral. Of this latter, the angular integrations are carried out and are presented in tabular form. Its radial integrals are the same as those of Slater. In addition to giving interval relations in (jj) coupling, the results help to solve the problem of determining the levels of a configuration for general coupling.

99. Many electron transitions. S. GOUDSMIT AND L. GROPPER, *University of Michigan.*—First and higher order perturbation terms of the spin-orbit and electrostatic interaction in the eigenfunctions of many-electron configurations explain the occurrence of many-electron transitions. By considering which terms can occur in first order perturbation the following selection rules were obtained. No more than three electrons can jump at a time. (a) When three electrons jump all can change their n by an arbitrary amount, one changes its l by ± 1, the others by δ and ϵ, $\delta+\epsilon$ being even. (b) When two electrons jump both can change their n arbitrarily, one changes its l by $\delta \pm 1$, the other one by ϵ. Breaking off the series expansion for $1/r_{ij}$ in the electrostatic interaction after the second term gives for δ and ϵ only the values $0, \pm 1$. The Heisenberg two-electron selection rule is therefore to be considered as a special case of (b). Qualitative rules have been derived to tell when many-electron transitions may be strong. Special selection rules were found for (j, j) coupling. The first order terms also cause anomalies in the intensities of one-electron transitions.

100. The arc spectrum of rhenium. WILLIAM F. MEGGERS, *Bureau of Standards.*—The arc spectrum of rhenium has been photographed from 2100A in the ultraviolet to 8800A in the infra-red; it has more than 3,000 lines in this interval. About 25% of the lines show hyperfine structure of 2 to 6, or more, components. The centers of gravity of complex lines have been determined and are assumed to represent the effective wave-lengths for purposes of analysing the gross structure of the Re I spectrum. About 500 lines, including nearly all of the stronger ones, have been classified as combinations of terms belonging to quartet, sextet and octet systems. The normal state of the neutral Re atom is represented by $(5d^5 6s^2)a^6S_{2\frac{1}{2}}$. Series-forming terms have been identified which indicate that the ionization potential is approximately 7.8 volts.

101. Evidence regarding the structure of the arc and spark lines of nitrogen. P. G. KRUGER

AND R. C. GIBBS, *Cornell University.*—Nitrogen arc (NI) lines (λ's 6484, 4151, 4109, and 4099A) have been excited in a liquid air cooled condenser type discharge. These lines were photographically examined with the aid of a Fabry-Perot interferometer whose resolving power, depending on the spacing of the mirror surfaces, was 10^6 or better. With the resolution and dispersion thus obtained, the above lines were found to be sharp and lacking in any evidence of structure. The total line widths have been found to be 0.015, 0.011, 0.010 and 0.010A respectively. Nitrogen spark (N II) lines (λ's 3995, 4601, 4607, 4614, 4621, 4630, 4643, 5666, 5675. 5679, 5686 and 5710A) have been excited in a liquid air cooled electrodeless ring discharge. The microphotometer curves of the interference patterns from these lines show evidence of structure, although the components are so near together that they have not been clearly separated. The total line widths of these lines are three or four times as large as the widths of the arc lines. This gives added support to the conclusion that the spark lines are definitely complex.

102. The spectrum of Li III. H. G. GALE AND J. B. HOAG, *University of Chicago.*—In accordance with the simple Bohr theory, the spectrum of Li III should show lines analogous to the Lyman series at 135.0, 113.9, 108.0, 105.5, 104.2 etc., and lines analogous to the Balmer series at 729.1, 540.0 Angstroms, etc. We have succeeded in photographing and measuring on several plates five lines of the first of these series and the first line of the second. The line at 135A has been measured in three orders. The first two lines of the first series were previously measured by Edlén and Ericson. The third, fourth and fifth lines of the first series and the first line of the second series have not been previously reported. The $K\alpha$ line of lithium (199.26A) is very strong on many of the plates and has been measured in four orders. The vacuum spectrograph is the same as that first used by Hoag. (Astro. Jr. LXVI, 225, 1927). An electric furnace was used at first to produce lithium vapor between metallic poles. Better success has been obtained recently by using poles of lithium stanide and also metallic lithium in nickel holders.

103. Hyperfine structures in the first spectra of krypton and xenon. C. J. HUMPHREYS, *Bureau of Standards, Washington, D. C.*—The stronger arc lines of krypton and xenon have been examined for hyperfine structures. Methods of observation include the use of a Hilger Fabry-Perot interferometer having quartz plates of 6 cm aperture, a number of fixed étalons, and two quartz Lummer-Gehrke plates. The results obtained by different methods show very satisfactory agreement. Structures of the following lines have been measured: Krypton, 5570.2890, 7685.2472, 8059.5053, 8104.3660, 8281.11, and 8508.8736A; Xenon, 4193.5296, 4500.9772, 4734.1524, 8231.6348, 8409.190, and 8819.412A. No definite numerical regularities in the spacing of components, such as have been reported in the case of neon, have been observed, although with one exception the xenon lines showing structures are due to combinations with the low $^3P_2$ level and the pattern consists of four components. The satellites of neon lines are supposed to be due to Ne isotope, 22. Krypton and xenon are reported to have 6 and 9 isotopes respectively and the fine structure might be expected to be more complicated. The existence of a reported satellite of the krypton line, λ5570.2890A, has been confirmed. It is hoped that, by use of some cooling agent such as dry ice, additional structures may be resolved.

104. On the spectra of singly ionized rubidium and caesium. OTTO LAPORTE AND GEORGE R. MILLER, *University of Michigan.*—The spectra of Rb II and Cs II were investigated by means of a hollow cathode tube and a hot spark in the visible and ultra-violet regions. The data obtained were compared with the analyses of Reinheimmer (Ann. d. Physik **71,** 162, 1923) and Sommer (Ann. d. Physik **75,** 163, 1924) respectively. The classifications of these authors were found to be essentially correct though lacking greatly in completeness. The present analysis established the configurations $4p^6$, $4p^55s$, $4p^54d$, $4p^55p$, $4p^56s$ and $4p^55d$ in Rb II and of the corresponding configurations in Cs II. Spectrograms of the hollow cathode discharge of Rb II in the visible region are of special interest because the limit of excitation furnished by metastable helium falls exactly between the various levels caused by $4p^55p$, thus providing a check on the interpretation of the classification. The energy diagram of Cs II shows as a characteristic feature the decomposition of the levels of the above mentioned configurations into two distinct groups due to the large separation of $5p^5\,^2P$ of Cs III. The value of the ionizing potential of Rb II is 27.3 volts and that of Cs II 23.4 volts. Both values are about two volts larger than those given by Mohler (Phys. Rev. **28,** 46, (1926)).

105. Term values in the arc spectrum of selenium, Se I. R. C. GIBBS AND J. E. RUEDY, *Cornell University.*—A partial analysis of the arc spectrum of selenium has been given by Runge and Paschen (Astrophys. Jour. 8, 70, 1898) in the region 4700–7100λ, and by McLennan, McLay, and McLeod (Phil. Mag. **4,** 486, 1927) in the region 1400–2300λ. The present work is an extension of the data throughout the region 1300–9100λ, with the classification of a number of new lines. It has been found possible to determine the term values of certain levels built on the lowest level of Se II, $4p^3\,^4S_{3/2}$, and to relate them to this limit. The ionizing potential between the lowest level of Se I, $4p^4\,^3P_2$, and this limit has been computed as 9.70 volts.

106. Series in the spectrum of Germanium II. C. W. GARTLEIN, *Cornell University.*—High excitation of the first spark spectrum of germanium, Ge II, has been obtained in a Schuler lamp with circulating helium gas and a quantity of metallic germanium of high purity in a carbon cathode. The spectrum was photographed in the region 500A to 2500A with a vacuum spectrograph, from 2500A to 4000A with a 75 cm focus quartz spectrograph, and from 4000A to 9000A with a Zeiss 3 prism glass spectrograph. The series $4s^24p^2P^0_{\frac{1}{2},1\frac{1}{2}} - 4s^2nd^2D_{1\frac{1}{2},2\frac{1}{2}}$ has been obtained for values of n from 4 to 11, and five members of the series $4s4p^{2\,2}D_{1\frac{1}{2},2\frac{1}{2}} - 4s^2nf^2F^0_{2\frac{1}{2},3\frac{1}{2}}$ have also been obtained. From these data the series limit has been calculated to be 128,535 ± 50 cm^{-1} above $4s^24p^2P^0_{\frac{1}{2}}$ and gives about 15. 86 volts as the second ionization potential of germanium. Many new intercombination lines have been obtained. This work confirms the assignment of the low terms made by R. J. Lang (Phys. Rev. **34,** 696, (1929)) and shows the ionization potential to be slightly lower than the estimates of Lang and of Rao and Narayan (Proc. Roy. Soc. **A119,** 607, 1928).

107. A study of the vanadium I iso-electronic sequence. HELEN T. GILROY, *Cornell University.*—A study has been made of most of the spectra in the vanadium I iso-electronic sequence due to the possible electronic changes between the following configurations,—$3d^44s$, $3d^44p$, $3d^5$, $3d^44d$, $3d^34s^2$, $3d^34sp$. Application of the regular and irregular doublet laws to this sequence indicates that a five-electron system, giving quartets and sextets may be added to the systems studied by Bowen and Millikan and Gibbs and White, all of which obey these laws. To illustrate the regular doublet law one $\Delta\nu$ between sextet or quartet levels has been selected from each electronic configuration and $(\Delta\nu/K)^{1/4}$ calculated. The increase in $(\Delta\nu/K)^{1/4}$ is nearly linear with increase in atomic number. Screening constants obtained from these same 'doublets' vary from 16.18 to 15.05 through the sequence from vanadium to cobalt. Moseley diagrams have been drawn for sextets and quartets from each configuration. Utilizing the values of the vanadium I and chromium II limits as estimated by Russell, square roots of term values $(\nu)^{1/2}$ were computed and plotted against atomic number for sextets and quartets. Wherever the electron change did not involve a change in total quantum number $\Delta(\nu)^{1/2}$ was found constant through the sequence to Ni VI.

108. Possible direct reading methods for measuring the current in the electrodeless discharge. CHAS. T. KNIPP, *University of Illinois.*—An inductive method is described for measuring the magnetic component of the electrodeless discharge. In this the gaseous electric current circulating through a reentrant discharge tube was piped, so to speak, aside where it made a loop of one turn and then returned. A low resistance coil of one turn of heavy braid copper wire was placed in the maximum inductive position about this loop. Its terminals were connected to a radio ammeter. With this arrangement the ammeter, on excitation of the electrodeless discharge, read 3 amperes. Further, replacing the ammeter by a 5 cm bridge of No. 38 Ni wire, the wire instantly was fused; and, finally, an aluminum disc suspended within the loop, by a thread attached to its edge, and with its plane parallel to the gaseous current set itself briskly at right angles to same. The magnitude of these effects came as a surprise. The energy was supplied by a 25 kv., 800 kc motor-generator set, which gave highly damped waves.

109. Electrodeless discharge characteristics of hydrogen and nitrogen. OTTO STUHLMAN, JR. AND HENRY ZURBURG, *University of North Carolina.*—Electrodeless arc discharges were obtained by means of a predominant electrostatic field in a spherical bulb placed in a long solenoid excited by undamped high frequency oscillations. Critical minimum potentials to strike the arc were obtained as a function of gas pressure for frequencies between 1.5 and 4.5 million cycles.

The characteristics conformed closely to Pashan's law. The critical points defined by the minimum values of X_m and P_m for a given frequency of excitation showed that the Log $(X/p)_m$ was a linear function of the frequency f, between discontinuities, interpreted as critical points of ionization. These critical ionization points were found to be interpretatable as arising through successive impacts. The results show that here as in Towsend's work at higher pressures X/p increases with decreases in p. X_m was found to decrease with increase in f except where the relation passed periodically through sharp maxima, indicating by their shapes differences in elasticity of impact between the two gases, nitrogen behaving like an inelastic gas and hydrogen like an elastic gas. Pressure-frequency relations indicated the existence of the same ionization discontinuities.

110. The ionization by electron impact and extra ionization potentials of nitrogen and carbon monoxide. JOHN T. TATE AND P. T. SMITH, *University of Minnesota.*—The total positive ion current in nitrogen and carbon monoxide has been measured as a function of the energy of the impacting electrons out to 750 volts. The number of positive charges per electron per cm path at 1 mm pressure of Hg and 0°C was calculated. The efficiency curves for the two gases are almost the same and are very similar to those obtained for the inert gases (Phys. Rev. **36,** 1293 (1930)) and Hg vapor (Phys. Rev. **37,** 808 (1931)). Nitrogen has a maximum efficiency of 10.25 ions at about 100 volts and carbon monoxide a maximum of 10.87 at 105 volts. Extra ionization potentials in nitrogen were found at 15.80 (first ionization potential), 16.01, 16.30, 16.45, 16.55, 16.68, 16.79, 16.88, 16.96, 17.08, 17.20 and 17.44 volts. In carbon monoxide they were found at 14.20 (first ionization potential), 14.36, 14.49, 14.61, 14.71, 14.82, 14.91, 15.36, and 16.38 volts.

111. Mobilities of Na^+ ions in H_2 as a function of time. LEONARD B. LOEB, *University of California.*—The mobilities observed for Na^+ ions from a Kunsman source in H_2 (Phys. Rev. **36,** 152 (1930)) lead to a study of the square wave-form oscillations used. These were shown to be unreliable above 5000 cycles. The previous observations were substantially confirmed with the square waveform tube oscillator and by commutator at low frequencies and by sinusoidal oscillations from two different sources and with two different approaches from 2000 to 40000 cycles. For times of ion transit greater than 5×10^{-4} seconds the mobility uncorrected for temperature was 16 cm/sec per volt/cm. From 10^{-4} to 10^{-5} seconds mobilities of 21 were observed. Between these times intermediate values were found depending somewhat on the purity of the gas. The density correction for gas temperature in the path is slightly uncertain. The average temperature lay between 115°C and 60°C, the best value being 80°C. The mobility constants for the values above are therefore 13.5 and 17.5 respectively. The normal values observed in H_2 from ionization processes are 8.4 cm/sec. The latter value has no significance as the nature of the positively charged molecular nucleus of the ion is not known. The 17.5 value possibly corresponds to the Na^+ ion, while the 13.5 cm/sec value corresponds to a Na^+ ion with an attached molecule.

112. Evidence of energy exchanges accompanying scattering of atoms by crystals. H. A. ZAHL AND A. ELLETT, *State University of Iowa.*—The distribution of mercury atoms scattered from NaCl, KCl, KBr, KI has been studied by means of an ionization gauge as a function of angle of incidence and temperatures of scatterer and incident beam. The direction of maximum intensity makes an angle with the crystal normal not equal to the angle of incidence but always slightly less. The distribution can be well represented by $A\cos\theta+B\cos m(\alpha-\theta)$ ($B=0$ when $|m(\alpha-\theta)|>\pi/4$). The departure from specular reflection $\gamma=$(angle of incidence $-\alpha$) is greatest for high incidence, being 16° to 4° at an angle of incidence of 70° and about 5° at 45°. The values of A/B, m and γ depend on temperatures of crystal and beam. For rock salt at least, γ is less (more nearly specular) the colder the crystal and hotter the beam. Since any incident beam gives rise to diffuse scattering ($A\cos\theta$) plus directed scattering $\{B\cos m(\alpha-\theta)\}$ centered about a line making a greater angle with the crystal surface than does the incident beam it follows that the scattering is accompanied by an energy exchange.

113. The dependence of reaction velocity on temperature. R. M. LANGER AND B. G. CALVERT, *Massachusetts Institute of Technology.*—In a reaction which goes according to the law

$N_E(t) = N_E(0)e^{-\lambda(E)t}$ where $\lambda(E)$ is an increasing function of the energy E, and $N_E(0)$ is the number of systems in state E given by Boltzmann's Law, there are three characteristic types of temperature dependence. (1) For low temperatures there is a range in which the temperature coefficient defined by Tolman's formula $(\overline{E^2}-\overline{E}^2)/kT^2$ is constant and exceedingly small. Then comes a region (2) where the temperature coefficient rapidly increases with temperature. For higher temperatures (3) the curve again flattens out and the reaction rate K which is an average of $\lambda(E)$ can be expressed in the form $K=(1/\tau)e^{-A/kT}$ where τ is of the order of the period of oscillation of the system. Enough is known about the function $\lambda(E)$ to show for example that in the case of ordinary chemical reactions the region of (3) has already set in far below room temperature and that τ is of the order of 10^{-14} sec. For the typical radioactive processes on the other hand the region of (1) extends above 10^6 degrees. The temperature coefficient at ordinary temperatures is about 10^9 times smaller than in the chemical case so that regardless of the closeness of energy levels in the nucleus and even if the nucleus were in thermal equilibrium which is not the case until very much higher temperatures) the difference in radioactive decay rate between 0° absolute and ten thousand degrees would be inappreciable $(\Delta K/K<10^{-4})$ even if there were no experimental difficulties in its determination.

114. Improved apparatus for temperature control. E. J. WORKMAN, *National Research Fellow, Bartol Research Foundation of the Franklin Institute.*—Temperature regulators involving the use of a grid controlled arc (thyratron) with a photoelectric cell and galvanometer *light* spot usually suffer from the effect of "hunting." This effect is inherent in the thermal capacity of the heated unit and is not reduced by increasing the galvanometer sensitivity. Such effects may be eliminated by placing in front of the photoelectric cell a rotating diaphragm having the form of an Archimedes spiral $[r(\text{inches})=1+0.08\theta]$. The rotating spiral is placed in such a position that the light from the galvanometer mirror falls intermittently on the photoelectric cell, and its duration of transmission is proportional to the galvanometer deflection. With the light beam intercepted in this way, the photoelectric cell causes a thyratron to give pulses of current of duration appropriate to the conditions of balance in the galvanometer circuit. This apparatus reduces the temperature fluctuations by a factor of from 10 to 50 times in comparison to the fluctuations obtained when the stationary diaphragm is used. Applications other than temperature control are discussed.

115. The isotopes of lithium, sodium and potassium. K. T. BAINBRIDGE, *National Research Fellow, Bartol Research Foundation, Swarthmore, Pa.*—Magnetic analysis of the positive rays of lithium from a spodumene source shows no change in the relative abundance of Li^7 and Li^6 with temperature. This is in agreement with Aston and Morand but at variance with the results of Dempster, Thompson, and the similar work of Hundley. A possible explanation of Hundley's results appears when the effects of space charge and the geometry of the tube are considered. In the present work, the ion currents were not limited by space charge, the ions when brought successively to the receiving slit described exactly the same path throughout, and the resolution was great enough to secure complete separation of the ion beams with freedom from background and strays. If Na^{21} or Na^{25} exist at all they are present to less than 1/3000 of Na^{23}. No evidence is secured of K^{40} or K^{42} to 1/300 to 1/1500 respectively of K^{39}. The presence of these isotopes has been predicted or suggested by Beck, Fournier, Kossel and others from nuclear regularities among the elements or to account for the radio-activity of potassium. The complete paper will appear in the Journal of the Franklin Institute.

116. The absorption coefficient for electrons in phosphorus and arsenic vapors. ROBERT B. BRODE AND METTA CLARE GREEN, *University of California.*—The absorption of electrons from a beam sent through the vapor has been observed for a range of electron velocities from 1 to 100 volts in phosphorus and from 4 to 200 volts in arsenic. In the phosphorus curve α has a minimum of about 345 cm^2/cm^3 at 2 volts, a maximum of about 380 at 4 volts, shows a definite decrease of slope around 16 volts and becomes about 150 at 100 volts. The actual magnitudes are not definite, due to uncertainties in vapor pressure data, to thermal effusion, and to transitions between yellow and red phosphorus during the measurements. No maxima or minima were observed in the arsenic curve. The values of α ranged from about 800 cm^2/cm^3 at 4 volts to about

250 at 200 volts. These values were taken using pressures from 1 to 3×10^{-3} mm of Hg. because outside these limits there were consistent departures from a linear relationship between log I/I_0 and pressure. At the temperatures and pressures used the molecular formulas are indicated by available data to be P_4 and As_4.

117. Neutralization and ionization of high velocity helium particles. PHILIP RUDNICK, *University of Chicago.* (*Introduced by A. J. Dempster.*)—A low voltage hot cathode arc and an accelerating potential were employed to produce high speed helium particles of homogeneous velocity corresponding to 7 to 22 kilovolts, which were then allowed to pass through helium gas. The equilibrium proportion of positive to neutral particles was found to increase with voltage in this range from 0.08 to 0.23. The mean free path for ionization of the high velocity neutral helium atom was found to vary approximately inversely as the square of the velocity from 19×10^{-4} cms to 6.5×10^{-4} compared with the kinetic theory mean free path of 17×10^{-4} cm. This is in agreement with Rüchhardt's hydrogen canal-ray measurements but differs from the behaviour of α particles where free path for change from single to double charge increases with the velocity. The mean free path for neutralization of the positive ions was computed to be 1.4×10^{-4}, practically independent of the velocity. The probability of capture of electrons by α rays has been found to depend very strongly on the velocity, in contrast to the approximate independence shown by these slower helium ions. These measurements were made by the method of Wien, with transverse electrostatic fields, using a thermocouple to detect the rays.

118. A method for producing high speed hydrogen ions without the use of high voltages. ERNEST O. LAWRENCE AND M. STANLEY LIVINGSTON, *University of California.*—A method for producing high speed hydrogen ions without the use of high voltages was described at the September meeting of the National Academy of Sciences. (Science **72,** 376 (1930).) The hydrogen ions are set in resonance with a high frequency oscillating voltage between two hollow semicircular plates in a vacuum, and are made to spiral around in semicircular paths inside these plates by a magnetic field. Each time the ions pass from the interior of one plate to that of the other they gain energy corresponding to the voltage across the plates. This method has now been tried out with the following results: Using a magnet with pole faces 10 cm in diameter and giving a field of 12,700 gauss, 80,000 volt hydrogen molecule ions have been produced using 2000 volt high frequency oscillations on the plates. A voltage amplification (the ratio of the equivalent voltage of the ions produced to the high frequency voltage applied to the plates) of 82 has been obtained. These preliminary experiments indicate clearly that there are no difficulties in the way of producing one million volt ions in this manner. A larger magnet is under construction for this purpose.

119. Photoelectric fatigue in cobalt. GEORGE B. WELCH, *Marshall College.*—The rate of photoelectric fatigue in cobalt, as a function of the incident radiation, is greater when a quartz-to-Pyrex graded seal is used on the apparatus than it is when the quartz window is attached with de Khotinsky cement. Sealing a side tube containing de Khotinsky cement into the apparatus causes the rate of fatigue to decrease. With nitrogen in the cell, the customary fatigue effects were observed. These experiments were made with pressures ranging from 10^{-7} to 10^{-5} mm of mercury, using the method described by the writer (Phys. Rev. **32,** 657 (1928)). Within these limits, an increase in pressure increases the rate of fatigue, an observation which receives some confirmation in experiments performed with electrolytically deposited sodium cells. An explanation is made on the basis of the "patch" theory. (Acknowledgment is made to the National Research Council and to Cornell University for material assistance in this work.)

120. Photoelectric effect of caesium vapour. F. W. COOKE, *University of Illinois.*—The measurements reported by Mr. E. M. Little, (Physical Review **30,** 109, (1927)), have been continued with a view to explaining the difference between the results of Little and F. L. Mohler. No effect has been found on the long wave-length side of the critical wave-length 318.4$\mu\mu$. The effect is a maximum at this convergency frequency, decreases with increasing frequency, reaches a minimum and begins to increase again. The order of magnitude of the effect is the same as that of Mohler. Several disturbing effects had to be eliminated and the final effect was only obtained as a difference between a dark current and the current due to light.

121. Intensity of infrared absorption bands. LORNE A. MATHESON, *University of Michigan.*—The intensity of absorption bands of gases in the near infrared has been determined by a new method. A beam of radiation of known spectral intensity is passed through the absorbing gas and the absorbed energy found by its resulting heat production causing a measurable expansion of the gas. Readings for various concentrations of absorbing gas are extrapolated to zero concentration. From the results one may calculate the matrix component of the electric moment corresponding to the vibration transition causing the band and the line width of the individual lines. Preliminary results have been obtained with CO.

122. Infrared absorption bands in formaldehyde vapor. HAROLD H. NIELSEN AND JOHN R. PATTY, *Ohio State University.*—Two of the principal regions of absorption in Formaldehyde vapor reported earlier at 3.5μ and 4.7μ have been further investigated with an echellette grating with a spacing of 3600 lines to the inch. The region at 3.5μ, earlier thought to be a band consisting of P, Q and R branches has been found under higher dispersion to consist of three overlapping bands with centers at 3.61μ, 3.52μ and 3.37μ. Two of these (3.61μ and 3.37μ) show P, Q and R branches. The average spacing between lines in these bands is about 3.5 cm^{-1}. The third band (3.52μ) has only one branch which constists of groups of closely spaced lines. The spacings between these groups is about 14.0 cm^{-1} or about four times that of the other bands. The region at 4.7μ is similar to those at 3.6μ and 3.37μ in spacing and structure. Due to better resolution in this region, what at 3.37μ appeared as a single line here appears as a group of very closely spaced lines incompletely resolved. Calculations on molecular models of slight asymmetry show very good agreement between theory and experiment for the case where the principal moments of inertia have the values: $A_x = 2.7\times10^{-40}$, $A_y = 18.0\times10^{-40}$, $A_z = 21.0\times10^{-40}$ gm-cm^2.

123. The visible and ultraviolet absorption spectra of certain amino acids and their significance. GLADYS A. ANSLOW AND MARY LOUISE FOSTER, *Smith College.*—The absorption spectra of the acid solutions of alanine, cysteine, aspartic acid, glutaminic acid, and cystine have been studied from 650 to 200 $m\mu$ with a rotating sector photometer. Aspartic and glutaminic acids, whose molecules are nearly symmetrical about the bond between the α and β carbons, gave broad, structureless bands in the visible region with maxima at 526 and 495 $m\mu$, respectively, probably caused by vibration in this bond. Cystine showed a narrower band with maximum at 251 $m\mu$, which is ascribed to vibration in the *S-S* bond, about which it is symmetrical. Continuous absorption started in all the acids between 225 and 200 $m\mu$, due to dissociation in a common group, the least energy being required to dissociate the heaviest molecule. The energy of dissociation in volts is 5.46, 5.52, 5.62, 5.75, and 6.07 for cystine, glutaminic acid, aspartic acid, cysteine, and alanine, respectively. This dissociation probably occurs in the carboxyl group, for similar compounds, lacking the amino group, give continuous spectra in the same region, as was also found by Ley and Hünecke (Ber. Deut. Chem. Gesel. **59**, 510, 1926). Since the water solutions give like spectra except for a slight shift to shorter wave-lengths, the carboxyl group must be present in the same form in acid and water solutions, contrary to the zwitterion theory.

124. The fundamental vibration bands of CO_2. P. E. MARTIN AND E. F. BARKER, *University of Michigan.*—The absorption bands of CO_2 at 4.3μ and 14.9μ have been examined with a grating spectrometer of resolving power sufficient to separate the rotation lines. The 4.3μ band consists of positive and negative branches only, with rotation lines about 1.5 cm^{-1} apart, and shows considerable convergence. The spacing is the same as in the long wave band, and is about twice the value obtained when estimated in the usual way from the doublet separation. This indicates that the molecule is linear, with the carbon atom midway between the two oxygen atoms. In the low frequency band a strong zero branch appears at 14.9μ, with twenty or more rotation lines on either side, about equally spaced. The motion associated with this band is one in which the carbon atom vibrates in a plane normal to the line adjoining the two oxygen atoms. A second harmonic band appears at 4.8μ, but there is no first harmonic. Superposed upon the fundamental are three other bands, considerably less intense, of which two correspond to absorption by molecules already excited to the first vibration state by thermal impacts, while the third is a difference band involving the inactive symmetrical vibration. The energy values for three of the vibration states associated with the lower frequency may thus be determined, and

these yield precisely the Raman frequencies observed by Dickinson, Dillon and Rasetti, interpreted as transitions of two in the vibrational quantum number which are required by the selection rules for this isotropic vibration.

125. The vibration spectrum of the N_2O molecule. E. K. PLYLER AND E. F. BARKER, *University of Michigan.* Three very intense infrared bands which apparently correspond to the fundamental vibrations of the N_2O molecule have been observed at wave lengths of 16.9μ, 7.7μ and 4.5μ. All three have been resolved under high dispersion, the rotation lines in each case being spaced about 0.8 cm^{-1} apart. The band at 16.9μ has a strong zero branch, while the other two are of the doublet type. The three first harmonics have also been found, and the one at 8.6μ resolved. This latter is a doublet type band although its fundamental has a zero branch. In addition to these, five combination bands have been studied, all but one being of the doublet type. Several of the bands are complicated by the superposition of absorption due to molecules already excited to the first or second vibration state for the lowest frequency.

126. The band spectrum of germanium sulfide. C. V. SHAPIRO, R. C. GIBBS AND J. R. JOHNSON, *Cornell University.*—A band spectrum of germanous sulfide (GeS) has been observed in absorption at temperatures between 450 and 550°C, in the region λ3300 to λ2400. Two electronic transitions have been observed, originating from the same normal state of the molecule. The equations for the band heads are:

$$\text{I.} \quad \nu = \nu_e(\text{I}) + 378.2(v' + 1/2) - 1.55(v' + 1/2)^2 - 580.2(v'' + 1/2) + 3.2(v'' + 1/2)^2$$

$$\text{II.} \quad \nu = \nu_e(\text{II}) + 309.6(v' + 1/2) - 1.3(v' + 1/2)^2 - 580.2(v'' + 1/2) + 3.2(v'' + 1/2)^2$$

v' progressions of 13 and 9 members respectively have been followed in these systems, while v'' takes on values from 0 to 4. The intensity distribution is normal. There are indications of an isotope effect, as most of the heads are accompanied by two satellites, whose intensity is comparable to that of the main head, corresponding to the fact that germanium consists chiefly of three isotopes. These satellites are being investigated further. Extrapolation of the vibrational series of the two upper levels indicates that the products of dissociation are the same for the two. Assuming that normal atoms are produced by dissociation from the normal state, 3.7 volts are obtained as the upper limit for the energy of one or both of the atoms resulting from dissociation from the excited state of the molecule. This value is of the order of magnitude to be expected for the (still unknown) $^1S_0$ level of the basic configuration, $3s^23p^4$, of sulfur.

127. Zeeman effect in the $^2\Sigma - {}^2\Sigma$ cyanogen bands. E. L. HILL, *University of Minnesota.*—Interpreting the doublet separations in the lower state of these bands as due to a molecular magnetization by rotation, as suggested by Kemble, preliminary calculations have been made of the expected widths and intensity distributions of the Zeeman patterns of some of the doublets for various strengths of the magnetic field. The results indicate that for fields of about 8500 gauss a representative doublet such as λ3796.104 −0.184 should be unobservable as two lines, which seems at variance with the experiments of A. Bachem (Zeits. f. Physik **3,** 372 (1920)). For somewhat lower fields there may be complete or partial separation of the doublets. Further experiments are being conducted by Dr. Crawford at Harvard to determine with greater accuracy the form of the components of the doublets in the field. Assuming a suitable doublet separation in the upper $^2\Sigma$ state it seems possible that the rapid convergence of the predicted patterns might be checked, but there is at present no estimate of the magnitude of the no-field doubling for this state. If the experimental data seem to justify the effort, a more complete study of the Zeeman effect for Σ states will be undertaken.

128. Interpretation of the spectrum of BaF. A. HARVEY (*Commonwealth Fund Fellow*) AND F. A. JENKINS, *University of California.*—Observed in the first order of the 21-foot grating, the absorption spectrum of BaF presents some 200 bands heads in the region 3600–9000A. These represent all of the band systems previously known in emission, and two additional ones. The electronic levels, and the vibration frequencies, $\omega_{1/2}$, (in parentheses) are as follows: X, 0 (465.4); A, 11,630 (434.2); B, 12,260 (433.8); C, 14,040 (420.7); D, 19,990 (452.5); E, 20,190 (454.5); F, 24,170 (504.6); G, 26,240 (501.8). The systems $A \leftarrow X$ and $B \leftarrow X$, discovered in emission by Querbach, are evidently the components of the $^2\Pi \leftarrow {}^2\Sigma$ system analogous to that in

SrF and CaF, while the $C \leftarrow X$ system represents the $^2\Sigma \leftarrow {}^2\Sigma$ system also found for these molecules. $D \leftarrow X$ and $E \leftarrow X$ probably form a doublet system, which, by analogy with the Cs atom, would involve a more excited $^2\Pi$ level. The new systems $F \leftarrow X$ and $G \leftarrow X$ each consist of single-headed bands. New sequences in the $D \leftarrow X$ and $E \leftarrow X$ systems confirm Johnson's vibrational analysis, but Querbach's assignments in the infra-red system are corrected in important respects. All the bands resemble closely those of the isoelectronic molecule LaO, and here also the normal state must be the common lower level of all the known systems.

129. Boron hydride bands. R. F. Paton and G. M. Almy, *University of Illinois.*—Two bands due to boron hydride have been photographed in the spectrum of a 110-volt d.c. arc in hydrogen with amorphous boron contained in a nickel or copper cup as one of the electrodes. The bands obtained are those recently reported by W. Lochte-Holtgreven and E. S. van der Vleugel (Nature, Feb. 14, 1931) as the (0, 0) and (1, 1) bands of a $^1\Pi \rightarrow {}^1\Sigma$ transition in BH. They consist of P, Q, and R branches degraded to the red. The conspicuous Q heads are at λ4331 (0, 0) and λ4367 (1, 1). From the P and R branches the molecular constants obtained are $B_0' = 11.920$, $B_0'' = 11.808$, $B_1' = 11.21$, $B_1'' = 11.44$, $D_0' = -0.00143$, $D_0'' = -0.00118$, $D_1' = -0.0017$, $D_1'' = -0.00145$. These values indicate that the (0, 1) band should degrade rapidly to the violet. A careful search on our heaviest exposures failed to give definite evidence of such a band. The isotope band due to $B_{10}H$ was observed through the greater part of the P and R branches of the (0, 0) band and establishes the identity of the carrier. Microphotometer comparisons on three plates of the intensities of the 7 best lines in the R branch gave the abundance ratio of B_{11} to B_{10} as $4.86 \pm .15$, indicating an atomic weight of $10.841 \pm .005$, in good agreement with the chemical determination.

130. A further study of the emission spectrum of CO_2. H. D. Smyth and T. C. Chow, *Princeton University.*—The analysis of the CO_2 bands reported at the New York meeting has been considerably extended. We have now found combinations between the set of vibration terms previously reported ($\nu = \nu_0 + 1101.7v + 1.7v^2$) and eight or more levels of a different electronic state. This second set of levels seems to be made up of a double vibration set and seven of them can be fitted by a simple quadratic formula of the type

$$\nu = \nu_0 + a_1 b_1 + b_1 v_1^2 + a_2 v_2 + b_2 v_2^2 + b_{12} v_1 v_2$$

where the constants a_1 and a_2 are of the same order of magnitude as the Raman frequencies of CO_2. Though nearly a hundred bands have now been fitted into the scheme there remain numerous anomalies which we hope may be removed by further adjustment of the numerical constants. We are also endeavoring to get in emission the bands observed by Leifson in absorption and for this purpose are setting up a small fluorite vacuum spectrograph separated by a fluorite window from the excitation chamber previously described.

131. Band spectrum of bismuth chloride. Paul G. Saper, *University of Chicago.* (*Introduced by Robert S. Mulliken.*)—A band system of BiCl in the region from about 4300 to 5500A was excited by introducing vapor from heated $BiCl_3$ into active nitrogen. The bands are degrated toward longer wave-lengths. No other bands were found besides this system. The vibrational isotope effect showed that BiCl was the emitter. The isotope effect also served as a valuable aid in locating the origin of the system. The heads were measured and a vibrational analysis made. From the analysis an equation was obtained for the wave numbers of the $BiCl^{35}$ heads. Coefficients for an equation for the $BiCl^{37}$ heads were computed from theory from those of the $BiCl^{35}$ equation. These equations are given below.

$$BiCl^{35}: \nu = 21802.1 + [221.2(v' + \tfrac{1}{2}) - 308.6(v'' + \tfrac{1}{2})] - [2.65(v' + \tfrac{1}{2})^2 - 0.95(v'' + \tfrac{1}{2})^2]$$
$$BiCl^{37}: \nu = 21802.1 + [216.0(v' + \tfrac{1}{2}) - 301.4(v'' + \tfrac{1}{2})] - [2.53(v' + \tfrac{1}{2})^2 - 0.91(v'' + \tfrac{1}{2})^2]$$

The average difference between calculated and observed frequencies was ± 1.7 cm^{-1}. The isotopic displacement was calculated for the heads in the cases where the effect was evident, and a close agreement was found with corresponding observed values of the displacement.

132. Perturbations in the helium band spectrum. G. H. Dieke, *The Johns Hopkins University.*—A large number of electronic terms of the He_2 molecule is known, and therefore

its spectrum is especially suited to test the theory of perturbations developed mainly by Kronig. Two levels which lie close together perturb each other if they have: 1. The same J, 2. The same inversion symmetry, 3. The same exchange symmetry, 4. Λ different by at most ± 1, 5. The same multiplicity, 6. Approximately the same internuclear distance. The $ns\Sigma$ and $nd\Sigma$ levels of the He_2 molecule satisfy conditions 1. to 6. Rotational levels having the same J lie close together for $J=17$ if $n=4$, for $J=9$ if $n=5$, for $J=5$ if $n=6$. [n, total quantum number.] All these levels show marked perturbations which show in the spectrum by a displacement of the lines in question and sometimes by abnormal intensities. The two levels involved are shifted in opposite directions as required by the theory. There are numerous cases in which levels of the He_2 molecule come close together which do not satisfy the above conditions. Then there is no trace of any perturbation.

133. The effect of temperature upon the ultraviolet band spectrum of ozone and the structure of this spectrum. OLIVER R. WULF AND EUGENE H. MELVIN, *Bureau of Chemistry and Soils, Washington, D. C.*—The ultraviolet absorption of ozone in the region 3400−2300A consists of a large number of bands appearing against a background of continuous absorption. The effect of temperature upon this spectrum has been studied over the range −78° to 250°C. A definite though small effect has been observed. Grossly it manifests itself as an increase in contrast with decreasing temperature. Photometric results show this to be chiefly a decrease in absorption between the band edges, all of the bands appearing to come from normal vibrational levels of very low if not the lowest energy. Though somewhat diffuse, the bands tend to degrade to the red. The observed influence of temperature can be explained as the decrease of intensity in the higher rotational absorption of the bands, and possibly also in the continuous background, with decreasing temperature. Discontinuities in the intensity relations and the regular spacing of certain of the bands have led to a partial vibrational analysis indicating two active vibrational degrees of freedom in the excited electronic state. The observed change in the absorption with temperature may affect somewhat the estimates which have been made of the amount of ozone existing in the upper atmosphere.

134. Rotational analysis of the first negative group of oxygen (O_2^+) bands. DANIEL S. STEVENS, *University of Chicago.* (*Introduced by R. S. Mulliken.*)—The bands were produced by a hollow cathode discharge and photographed in the second order of 21-foot Rowland grating. The following bands were used in the analysis: 1–6; 0–6; 1–7; 0–7. As was expected these bands correspond to $^2\Pi \rightarrow {}^2\Pi$ transition like the double headed β bands of NO, the two molecules being alike in their electron configurations. The lower $^2\Pi$ is case a as in NO. Unlike the case of NO, however, the upper $^2\Pi$ is case b. The lower $^2\Pi$ is regular, with a doublet separation (corrected to zero rotation) of 195 cm^{-1}. Each band consists of eight branches (four P and four R) together with some indications of four weak Q branches. This is in agreement with theory. Alternate levels in each Λ-type rotational doublet are missing in both the upper and lower $^2\Pi$ states. This is as predicted by the quantum theory of homopolar molecules, since it is known that the nuclear spin of the oxygen atom is zero. The constants of the molecule in the two electronic states are given by: $B'=1.043-0.027v'$ cm^{-1}, $B''=1.583-0.009v''$ cm^{-1}, $r_e'=1.41\times10^{-8}$ cm, $r_e''=1.15\times10^{-8}$ cm.

135. Electronic energy levels of neutral and ionized oxygen. ROBERT S. MULLIKEN, *University of Chicago.*—The normal state of O_2 is known to be a $^3\Sigma_g^-$, probably corresponding to an electron configuration $\cdots 3d\sigma^2 2p\pi^4 3d\pi^2$ hereafter called A. The upper state of the Schumann-Runge bands is a $^3\Sigma_u^-$ probably derived (Herzberg) from $\cdots 3d\sigma^2 2p\pi^3 3d\pi^3$, hereafter called B. Configuration A should also give two metastable levels $^1\Delta_g$ and $^1\Sigma_g^+$, and B a set of metastable levels $^3\Delta_u$, $^1\Delta_u$, $^3\Sigma_u^+$, $^1\Sigma_u^+$, and one non-metastable level $^1\Sigma_u^-$. The upper level of the atmospheric bands, previously identified as the metastable $^1\Sigma_g^+$, is more probably the $^1\Sigma_u^-$. If it were $^1\Sigma_g^+$, the bands would be an intersystem quadrupole transition and probably much weaker than they are. (That $^1\Sigma_u^-$ of B should be below $^3\Sigma_u^-$, as here assumed, is indicated by consideration of the wave-functions.) The numerous bands observed by McLennan and others in liquid oxygen probably represent transitions to various metastable levels mentioned above. Or possibly some of these and the $^1\Sigma_u^-$ may belong to some other configuration, e.g. $3d\sigma^2 2p\pi^4 3d\pi 3p\pi$.

The normal and excited $^2\Pi$ states of O_2^+ (cf. preceding abstract) probably result from the respective removal of a $3d\pi$ or a $2p\pi$ electron from A. Existing data on O_2 and O_2^+ bands indicate 11.7 volts as the most probable value of the minimum ionizing potential of O_2.

136. Magnetic rotation spectrum and heat of dissociation of Li_2. F. W. Loomis and R. E. Nusbaum, *University of Illinois.*—The green magnetic rotation spectrum has been obtained from lithium contained in a nickel tube which was heated to about 1200°C by a low voltage stepped-down current. The tube was mounted in a solenoid which produced a field of 1300 gauss. The phenomenon can be seen in greater detail than in the previously studied spectra of Na_2 and K_2. In addition to the strong line at the head of each band caused by the piling up of the R branch lines, one can see the first few lines of the P branches of the strongest bands. Bands due to the lighter isotope are also visible. The spectrum extends to much higher values of v' and v'' than Wurm or Harvey and Jenkins report in absorption. It has consequently been possible to deduce a much improved value for the heat of dissociation. The frequencies of the magnetic rotation lines are represented by the following formula:

$$= 20398.4 + (266.90v' - 2.840v'^2 - 0.0637v'^3) - (349.00v'' - 2.605v''^2 - 0.0097v''^3).$$

The heat of dissociation deduced by extrapolation of the upper set of levels with a slight correction, due to the deviation of the highest observed levels from the formula, is 1.14 volts. Since the upper levels have been followed to within 0.1 volt of convergence this figure can hardly be in error by more than about 0.03 volt.

137. Valence forces in lithium and beryllium. J. H. Bartlett, Jr., and W. H. Furry, *University of Illinois.*—By methods similar to those used by Heitler and London, an investigation has been made of the interaction of two normal lithium atoms, and also of the interaction of two normal beryllium atoms. In the first case, two states, one attractive and the other repulsive, are possible for the molecule. The influence of the K shells has been neglected, and a nodeless wave function such as used by Guillemin and Zener (Zeits. f. Physik **61,** 199 (1930)) has been employed. The heat of dissociation of Li_2 is calculated to be 1.12 volts and the equilibrium internuclear distance to be 2.4A as against the experimental values of 1.14 volts (Loomis and Nusbaum, unpublished) and 2.67A, respectively (Harvey and Jenkins, Phys. Rev. **35,** 789 (1930)). No stable state is possible when two normal beryllium atoms interact with each other. A study is being made to ascertain under what conditions stable beryllium molecules will be formed.

138. Evidence against the existence of a chlorine isotope of mass 39. Muriel Ashley and F. A. Jenkins, *University of California.*—From results on the infrared spectrum of HCl, Becker (Zeits. f. Physik **59,** 601 (1930)) concluded that Cl^{39} exists in small amounts, in addition to Cl^{35} and Cl^{37}. A favorable opportunity for confirming this result is found in the ultraviolet absorption bands of AgCl analysed by Brice. The region adjacent to the $AgCl^{37}$ head of the 0.1 band is exceptionally free from structure, and the $AgCl^{39}$ head should appear at high vapor densities, if this isotope exists. The bands have been photographed with the 21-foot grating, using various vapor densities, from that at which the first appreciable absorption of the $AgCl^{37}$ head begins (550°C), to that for practically continuous absorption (850°). No trace of the predicted band was found. Using the vapor pressure data of Vartenberg and Bosse, the densities at the above temperatures are in the ratio 1/1000, and hence Cl^{39} cannot be present to a greater extent than 1/1000 of Cl^{37}, or 1/4200 of the whole. Similar investigations of the AgBr and AgI bands show that none of the elements involved possess heavier isotopes in quantities detectable by this method. For AgBr, the vapor pressure data of Jellinek and Rudat yield 1/2500 as the upper limit for a Br isotope of mass greater than 81.

139. The λ3360 band of NH. R. W. B. Pearse, *Commonwealth Research Fellow, University of California.*—The band at λ3360 emitted by the molecule NH (so-called "ammonia" band) has been photographed in the second order of the twenty-one foot concave grating for the purpose of remeasurement. The source used was a water-cooled discharge tube of large current carrying capacity containing a mixture of hydrogen and nitrogen. With the dispersion of

1.3 A/mm which was obtained the closely crowded line structure of the central maximum of intensity could be to a large extent analysed into the three components of a triple Q-branch. The band shows the three P, three Q and three R branches appropriate to a $^3\Pi \rightarrow {}^3\Sigma$ transition where the $^3\Pi$ state is near Hund's case b. The rotational term differences are obtained from these branches and used to evaluate the molecular constants. The improved wave-length data giving rise to improved values of these constants.

140. On the resolving power of the concave grating. J. E. MACK AND J. R. STEHN, *University of Wisconsin.*—An expression for the resolving power of the concave grating has been obtained, taking into account the fourth order effect upon the phase, of the departure of the grating from the plane. The result is expressed in terms of the "effective width" of the grating; i.e., the width of plane grating which gives the same resolving power as the concave one under consideration. This effective width is equal to the actual width, for narrow gratings. It increases to a maximum as the width of the grating is increased, then it decreases again and oscillates about a constant value, so that there is an optimum width, depending on the radius of the grating ρ, the angle of incidence ϕ, the wave-length λ, and the order of the spectrum. Of special interest is the case of grazing incidence (which has recently become important in extreme ultraviolet spectroscopy), where the effective width can never be greater than $2.3[\rho^3\lambda \cos \phi]^{1/4}$, and approaches a value 20 per cent less, as the width of the grating is increased. In actual cases the optimum width may be as small as 1 cm.

141. Reflecting power and grating efficiency in the extreme ultraviolet. H. M. O'BRYAN, *The Johns Hopkins University.*—By using a lightly ruled concave glass grating with a water-cooled vacuum spark between tungsten electrodes, enough intensity has been obtained to make quantitative measurements of grating efficiencies and reflection coefficients for various angles of incidence between 1000A and 280A in a vacuum spectrograph. To obtain the reflection coefficients, a mirror of the substance to be examined was rotated about the axis of a cylindrical oil-coated film on which the reflected spectra was photographed. Small gratings were inserted in place of the mirror with their rulings perpendicular to those of the concave grating and the spectra of the crossed gratings examined. Lightly ruled glass gratings, which were good at normal incidence, gave only extremely faint spectra near grazing incidence. Glass gratings etched with hydrofluoric acid were of little value at normal incidence but surprisingly efficient near grazing incidence. A grating of the echelette type, with the angle between the incident light and reflecting face of the groove made small enough to utilize the increased reflecting power at small angles will be the most efficient grating for the extreme ultraviolet and soft x-ray regions. The etched glass gratings approximate an echelette with a wide V-shaped groove.

142. Three methods of studying capillary structure as applied to wood. ALFRED J. STAMM, *Chemist Forest Products Laboratory, U. S. Department of Agriculture.*—Three different physical methods for studying the capillary structure of porous materials are developed and applied to the study of the fine effective continuous capillary structure of wood. The three characteristic capillary properties measured are, (1) the ratio of effective capillary cross-section to the effective length, (2) the average effective capillary radius, and (3) the maximum effective capillary radius. Some of the important characteristics of the porous structure of wood are briefly presented in order to show that the major part of the void structure, the fiber cavities, have very little to do with the permeability of wood. The pores in the pit membranes which connect the adjacent fiber cavities are shown to be the structure effective in controlling permeability of wood. These pores in the pit membranes in general, are below microscopic visibility, thus necessitating other means of study.

The ratio of the effective capillary cross-section to the effective capillary length is determined from electrical resistance measurements of strong salt solutions filling the void structure and from the specific resistance of the salt solutions in bulk. Strong salt solutions are used in order to make the surface conductivity negligible as well as the conductivity of the swollen cell wall. The average effective capillary radius is determined by combining the results of the preceding measurements with results obtained from hydrostatic flow studies of a continuous water phase extending through the section. Poiseuille's law is used for the calculations. A

differential pressure drop apparatus was devised for these measurements in which the flow of liquid through a standard capillary tube and the test specimen connected in series is determined by measuring the pressure drop through each. The maximum effective capillary radius is determined by measuring the gas pressure required to overcome the effect of the surface tension of water in the capillary systems. The data show the large differences between the fine capillary structure of heartwood and of sapwood.

143. The electric conductivity and dielectric constant of disperse systems. HUGO FRICKE, *The Biological Laboratory, Cold Spring Harbor, Long Island.*—This report refers in particular to suspensions of biological cells. The interior of a biological cell is a well conducting salt solution, but at its surface polarization or the presence of a non-conducting membrane obstructs the passage of an electric current with a resulting low conductivity and high dielectric constant of the suspension. The theory for the passage of an alternating current through a suspension of this type is dealt with and experimental work with various kinds of suspensions such as cream, wet sand, blood, and animal tissues, is described to show the applicability of the theory. The determination of the volume concentration of suspensions, of the form factor of the suspended particles, of the thickness of surface membranes, and of the interior conductivity of living cells are instances of practical applications.

144. Three component emulsions. P. G. NUTTING, *U. S. Geological Survey.*—A quartz sand grain, wet with water, tends to cling to oil but tends to remain on the water side of an interface. A glass plate, such as a microscope cover glass, may readily be floated on water if the water is first covered with gasoline. Muddy water, shaken with gasoline, is cleared, the particles of silt collecting in a tough skin at the interface. Muddy gasoline shaken with clear water gives the same result. Emulsions form whenever a dielectric fluid (air or an insulating oil), solid particles and a second fluid containing OH (water, alcohol, glycerine, linseed oil) are thoroughly mixed and allowed to stand. Two components give solutions and suspensions but never emulsions. The solid particles are supposed to adsorb OH ions on one side thereby acquiring an induced charge on the other which clings to the dielectric.

145. The electric mobility of proteins. HAROLD A. ABRAMSON, *Harvard University.*—I. The electric mobility of microscopic quartz particles covered with egg and serum albumins (crystallized 3×) is, between $pH=3.5$ to 5.5 (1) equal to the mobility of the dissolved protein molecules, and (2) proportional to the combining power of the proteins for acids and bases. This indicates that the amino and carboxyl groups of the adsorbed protein molecules are practically all oriented toward the aqueous phase. The method of mobilities, therefore, is a valuable means of studying the orientation of polar molecules at solid-liquid and liquid-liquid phase boundaries. This is further demonstrated by the behavior of crystals of tyrosine, cystine and aspartic acid. The electric mobilities of these particles indicate that the ampholytic nature of these substances is not simply responsible for the values of mobility. All these crystals are negatively charged at the isoelectric point calculated from the dissociation constants. All three have an isoelectric point at about $pH=2.4$, with reversal of sign in more acid solutions. The mobilities of the amino-acid crystals are, therefore, somewhat like those of inert surfaces, differing however in important respects. It seems likely that the amino and carboxyl groups at the surface of the crystal are not oriented toward the liquid.

II. The change in electric mobility of egg albumin with pH is proportional to the change in specific rotation. A method is available, therefore, for the comparison of change in potential with change in the rotation of the plane of polarized light.

146. The application of the ultracentrifuge to some colloid physical problems. J. B. NICHOLS, *E. I. duPont de Nemours & Company.*—Until recently there existed no very reliable method for determining particle-size distribution curves of colloidal material, especially lyophilic colloids. Accordingly a study was undertaken of the conditions required for undisturbed centrifugal sedimentation of fine-grained colloids and for the accurate determination of the sedimentation-velocity and diffusion relations. The present ultracentrifuge, as developed in Svedberg's laboratory, enables us to exert a centrifugal force 100,000 times that of gravity on a solution and thus to determine the particle size of a great variety of colloidal material and even

molecular weights of complex dyes or proteins. Valuable information can be obtained on phenomena such as the interaction of particles in solution, the effect of the environment on the state of aggregation, and Donnan potential effects.

147. The limitations and adaptability of ultramicroscopes to the study of colloid systems. L. V. FOSTER, *Bausch and Lomb Optical Co.*—Ultramicroscopes are of two distinctly different types. The best known is the cardioid ultramicroscope in which the illuminating portion produces a hollow cone of large angular aperture with its apex at the object. The observing system is a microscope consisting of a high aperture objective of angular aperture slightly less than that of the hollow cone and a high power eyepiece. The other is the slit ultramicroscope. The illumination system in the slit ultramicroscope is perpendicular to the observing system. Both systems are of high numerical aperture, but no direct light can enter the observation system. Details of construction of both types of ultramicroscopes and their sensitiveness of adjustment will be discussed. Expressions for their limitations in colloid microscopy will be given.

148. Physics in the study of pigment dispersions. F. A. STEELE, *The New Jersey Zinc Co., Palmerton, Pennsylvania.*—The study of colloids has reached the point where many important contributions are coming from physicists. Even more attention from physicists will be required if this science is to progress as it should. A suitable dispersion of zinc oxide in kerosene has a high yield value and marked plastic properties. A few drops of a dispersing agent added to this mixture largely destroys its plastic properties and greatly increases its fluidity. It is well established that the dispersing agent accomplishes this result by decreasing the interfacial tension and thereby destroying the flocculation of the pigment. In certain cases in paints, however, there is reason to believe an entirely different phenomenon is responsible for yield value and plasticity. Much work with the tools of the physicist is indicated in the solution of this problem. There is much to be done in the study of solid-liquid interfacial tension, adsorption layers, interfacial potentials, and the di-electric properties of colloids before these problems are to be solved. The behavior of pigments in rubber is also discussed.

149. Some theoretical aspects of the biological applications of physics of disperse systems. N. RASHEVSKY, *Westinghouse Research Laboratories, East Pittsburgh.*—A review of the author's recent theoretical work on the properties of small liquid drops and more generally of systems with very large specific surface, is given. When such a system interacts chemically with the surrounding, in such a way, that the mass of the substances, of which the system is constituted, slowly increases, the system will possess, under very general conditions, properties remarkably similar to those found in living organisms. Thus it is found that such a system may possess a positive rate of growth, when its size exceeds a certain critical one. Below this critical size the rate of growth is negative. Such a system therefore can never be formed spontaneously, although all substances necessary for its formation may be present. Under certain very general conditions such a system will, under the influence of osmotic and other forces, divide into two halves, when reaching a certain size, each half again growing and dividing, and so forth. In many cases the system will possess a very definite geometrical form, which will tend to be restored, when the system is deformed by some external disturbance.

150. Some colloidal properties of bentonite suspensions. H. A. AMBROSE AND A. G. LOOMIS, *Mellon Institute of Industrial Research and Gulf Research Laboratory, Pittsburgh, Pa.*—A study of the swelling and gelling properties of bentonite dispersions has been made in connection with the increasing use of this mineral for drilling oil wells. It is shown that the emulsoid type of colloids present responds to changes in the *pH* of the dispersion medium with respect to rate of settling, viscosity and swelling, thus behaving as a typical hydrophilic colloid. The curve for per cent of solid matter settled in a definite time as ordinate against the *pH* shows a maximum at the isoelectric point, with minima on each side of this point, corresponding to the points of maximum adsorption. As the *pH* is further increased or decreased flocculation begins with increased rate of settling. The viscosity curve is closely related to the rate of settling curve,

showing maxima and minima corresponding to the electro-viscous effect. Maximum swelling occurs at approximately the point of maximum viscosity. Methods are given for controlling the swelling of bentonites. Relaxation curves are given for bentonite suspensions and utilized to explain the suspension qualities of these sols for heavy mineral dispersions, such as barite or amorphous silica. A few applications of bentonite sols to the drilling of oil wells are given.

151. The theory of electrophoretic mobility. M. MOONEY, *United States Rubber Co., Passaic, New Jersey.*—The Helmholtz theory of electrophoresis is modified, in the case of a spherical particle, to take account of ionic diffusion, ionic mobility and the motion of the water. The effect of these factors on the charge distribution in the double-layer and on the electrophoretic mobility is calculated. The principal term in the resulting mobility formula applies to a sphere whose radius is infinitely greater than the mean thickness of the electric double-layer. It agrees with the Helmholtz mobility formula. A second term gives the first order correction for the curvature of the spherical surface. The Debye-Hückel theory of electrophoresis, the Helmholtz theory and the modified Helmholtz theory are compared; and it is shown that the different value for the numerical factor in the Debye-Hückel mobility formula results from a different assumption concerning the electric field in the immediate neighborhood of the particle when subjected to an external field. It is also argued, as a further consequence of this assumption, that the use of the Debye-Hückel formula is justified only at the other extreme in particle size, that is, for particles whose radii are small in comparison with the mean thickness of the double-layer. The experimental results of several investigators are considered in their connection with these theoretical deductions.

152. Wave motion and the equation of continuity. R. B. LINDSAY, *Brown University.*—The motion of a compressible fluid medium slightly disturbed from equilibrium is described by means of the two fundamental relations between ϕ, the velocity potential, and s, the condensation, viz., (A), the equation of *motion*: $\dot{\phi} = -c^2 s$, and (B), the equation of *continuity*: $\nabla^2\phi = -\dot{s}$. The elimination of either ϕ or s between (A) and (B) leads to the usual wave equation for propagation with velocity c. Now it is interesting that (A) focusses attention on the *motion* of a part of the medium which is considered to move as a whole (i.e., as a single particle), while (B) is the expression of the fact that a *continuous medium* is involved. Both ideas are thus implied in wave motion. The present paper studies several other cases where the combination of equations of type (A) and (B) leads to the wave equation. Such are, for example: (a) longitudinal waves in solid rods, (b) transverse waves along a flexible string (wherein, as in (a), the equation of continuity appears in the guise of Hooke's law), and (c), electromagnetic waves. As an allied matter of interest it is shown that equations of type (A) and (B) for a one dimensional continuum may be expressed in the form of generalized Hamiltonian canonical equations of motion where the Hamiltonian is replaced by a functional of ϕ representing the total energy in the medium. This further emphasizes the fundamental nature of equations of type (A) and (B).

153. Diffuse scattering of x-rays by simple cubic crystals. G. E. M. JAUNCEY AND G. G. HARVEY, *Washington University, St. Louis, Mo.*—The value of X in a previous paper by Jauncey (No. 68) has been determined for the case of a simple cubic crystal consisting of atoms of one kind and the formula obtained by Jauncey reduces to: $S=1+(Z-1)(f'^2/Z^2)-(F^2/Z)$. There are no experimental results for a crystal consisting of atoms of one kind, but Jauncey and May (Phys. Rev. **23,** 128 (1929)) have obtained values for the diffuse scattering of x-rays from a crystal of rocksalt. Assuming rocksalt to consist of atoms of atomic number (11+17)/2 or 14, we have calculated values of f' using values of F given by James and Firth (Proc. Roy. Soc. **A117,** 62 (1928)). These calculated values of f' are found to be only slightly greater than the values of F at absolute zero. Also Jauncey (Phys. Rev. **20,** 421 (1922)) has measured the effect of temperature on the diffuse scattering from crystals. From the above formula calculations of the ratio of the scattering at temperatures of 568° and 290°K have been made, using F values given by James and Firth. The theoretical and experimental values of this ratio in

one case are 1.29 and 1.33 respectively, and in another case are 1.13 and 1.18, thus showing good agreement between theory and experiment.

154. An experimental test of the ionization chamber method of measuring relative intensities of x-ray spectrum lines. SAMUEL K. ALLISON AND VICTOR J. ANDREW, *University of Chicago.*—A two-compartment ionization chamber has been constructed with the following properties (1) The fraction of the x-ray energy in the direct beam absorbed in the front compartment could be directly measured, (2) The volume of gas from which the ionic saturation current was drawn was sharply defined, (3) Fluorescent radiation or photoelectrons produced in the chamber could not reach the walls (4) The direct beam entered and left the chamber through thin windows and encountered no other parts of the chamber. The relative ionization currents produced in methyl iodide, methyl bromide, argon, sulphur dioxide, and air by the α_1, β_1, γ_1, lines of the tungsten L-series were measured and the ratios obtained after correction for fraction absorbed were found to vary not more than 1 per cent in the first four gases. In air a correction (Compton, Phil. Mag. **8,** 961 (1929)) must be made for scattering; if this is done, ratios agreeing with the first four gases were obtained. The results give strong support to the following hypothesis: The saturation current obtained from a given volume of any gas is proportional to the power of the fraction of the x-ray beam transformed into β-rays within it, providing the β-rays come to the end of their ionising range within the volume. Similar experiments on the uranium L-series are being completed.

155. Effects of ground faults and ground connections of the Wheatstone bridge. FRANK WENNER, *Bureau of Standards, Washington, D. C.*—The insulation outside the bridge proper may not be perfect, and with an alternating test current there may also be displacement currents between the source and detector leads. Either results in ground faults and requires that a correction be applied to the usual bridge equation or that certain auxiliary adjustments be made, and usually these adjustments involve some type of ground connection. Ground faults in each of the source and each of the detector leads increase the number of arms of the bridge from 4 to 8. While the equation for the 8-arm bridge is easily determined, usually a part of the data required for its use are lacking. It is shown, however, that the correction to the usual bridge equation necessary to take account of the effect of these ground faults can in most cases be determined from two additional balances of the bridge. One of these is made with one terminal and the other with the opposite terminal of the bridge grounded. Effects of other types of ground faults, and the effectiveness of various adjustments and ground connections in reducing the magnitude of the error resulting from ground faults in case a correction is not applied, are considered.

156. A new principle of sound frequency analysis. THEODORE THEODORSEN, *National Advisory Committee for Aeronautics, Langley Field, Virginia. (Introduced by J. S. Ames.)*—A new method of sound frequency analysis has been developed by the National Advisory Committee for Aeronautics in connection with a study of aircraft noises. The method is based on the well known fact that the ohmic loss in an electrical resistance is equal to the sum of the losses of the harmonic components of a complex wave, except for the case in which any two components approach or attain vectorial identity, in which case the ohmic loss is increased by a definite amount, even though the total current remains the same. This fact has been utilized for the purpose of frequency analysis by applying the unknown complex voltage and a known voltage of pure sine form to a common resistance. By varying the frequency of the latter throughout the range in question, the individual components of the former will manifest themselves, both with respect to intensity as well as frequency, by changes in the temperature of the resistance. No difficulties exist as to distortions of any kind. The fidelity of operation depends solely on the quality of the associated vacuum-tube equipment. An automatic recording instrument embodying this principle is described in detail.

157. The blackening of photographic plates by positive ions of the alkali metals. K. T. BAINBRIDGE, *National Research Fellow, Bartol Research Foundation, Swarthmore, Pa.*—The

blackening of Eastman x-ray plates has been measured as a function of the energy of the ions of Li, Na, K, Rb and Cs. The current density in the ion beam in the mass spectrograph was maintained at 1.32×10^{-8} amp/cm^2 for the most abundant isotope of each element. With exposures of one minute and for a density $D=0.3$ the energy of the ions ranged from 1440 electron-volts for Cs to 850 electron volts for Li^7. For a threshold density, $D=0.04$, the energy ranged from approximately 750 to 450 electron-volts for Cs and Li^7 respectively. A discussion is included of the probable mechanism of rendering a silver bromide grain developable, results with Schumann and Process plates, and blackening as a function of time and the intensity of the ion beams. The ion sources used, which are unsurpassed for steadiness, purity, and ease of manipulation, are described. The complete paper will appear in the Journal of the Franklin Institute.

158. The angular distribution of photoelectrons ejected by polarized ultraviolet light in potassium vapor. ERNEST O. LAWRENCE AND MILTON A. CHAFFEE, *University of California*—Light of wave-lengths in the region of 2400A selected by a monochromator and polarized by a pile of quartz plates illuminated a jet of potassium vapor. The lateral directions of emission of the photoelectrons relative to the electric vector were studied. Though the electrons were ejected with less than one equivalent volt velocity, the experiments were definite in establishing that the most probable direction of ejection is that of the electric vector and moreover that the angular distribution varies as the square of the cosine of the angle between the electric vector and the direction in question. This result is in accord with predictions of the wave mechanics for a spherically symmetrical atom and incidentally therefore constitutes additional evidence that molecules do not play an appreciable part in the observed photoionization of potassium vapor.

159. Λ-type doubling and electron configurations in diatomic molecules. ROBERT S. MULLIKEN AND ANDREW CHRISTY, *University of Chicago*.—Van Vleck's equations for the Λ-type doublet widths in $^2\Pi$ states, for all intermediate coupling cases between cases *a* and *b*, have been found to fit excellently the data on CH, OH, SiH, CaH, ZnH, CdH, HgH, etc. (Incidentally this had made possible a revision of the hitherto doubtful assignment of J values for the Q_2 lines in the $^2\Pi$, $^2\Sigma$ bands of CaH, and has permitted identification of the ^1R branch.) From the constants of these equations and similar constants for $^1\Pi$ and $^2\Sigma$ states, determined from empirical data, further confirmation of Van Vleck's theoretical results is obtained, also interesting information concerning electron configurations of molecules. In this way it is found that the n and l values previously assigned to outer electrons in hydrides have almost the same well-defined significance as they would in an atom formed by uniting the H nucleus with the heavier nucleus. For example, in the normal ($^2\Sigma$) and first excited ($^2\Pi$) state of CdH, with configurations $\cdots 5s\sigma^2 5p\sigma$ and $\cdots 5s\sigma^2 5p\pi$, the present evidence shows that the last electron really behaves like a $5p$ atomic electron, even though the normal ($^2\Sigma$) state is formed with a small energy of formation from a normal Cd atom ($\cdots 5s^2, {}^1S$) and a normal H atom ($1s, {}^2S$).

160. Colloid physics in latex technology. ANDREW SZEGVARI, *American Anode Inc., Akron, Ohio*. Latex, a suspension of rubber hydrocarbon (latex particles) in an aqueous solution, flows from the rubber tree in an extremely unstable state. When stabilized by raising the *pH* with ammonia it may be stored and becomes available for commercial purposes. The concentration may then be increased by centrifuging, creaming, or evaporation until 60 percent or more is rubber. Rubber goods may be made directly from such stabilized latex by electrodeposition, coagulation, ultrafiltration, evaporation, etc. The controlling factors in the deposition processes are the colloid physical conditions of dispersed systems and most eminently, the electrokinetic characteristics. The electrodeposition of latex gives an interesting colloid physical analogy to electrodeposition of ionic dispersed metals. The most striking difference between these systems with particles of such widely varying size, is the rate of deposition. This is considerably larger in colloid dispersed than in ionic dispersed systems. For most technological purposes the liquid latex systems must be compounded with conditioning ingredients. In this compounding the physical properties of suspensoid-dispersed systems are again concerned.

161. Dirac's spinning electron and Barnett's gyromagnetic effect. OTTO HALPERN, *New York University.*—The paper contains a treatment of the influence of a constrained rotation of the Dirac electron which may be free or bound to a nucleus. The proper values in the rotating system are changed as in the old quantum theory, the sum of spin and orbital angular momentum entering instead of the orbital momentum alone. There appear small additional terms of the order of fine structure separation times angular velocity of rotation.

162. On the design of high-tension condenser leads. HARRY CLARK, *Stanford University.*—A condenser was built for use at 50 kv on direct current consisting of several large glass plates coated with tinfoil and stacked together almost in contact in air. The leads were tinfoil strips 1 inch wide. Although each plate withstood a long test at 80 kv, the assembly sparked over at 50 kv. The discharge occurred opposite a lead where the minimum spark-length was 9 inches and was caused by the inductive effect of the lead and proximity of the plates. The defect was remedied without separating the plates by using leads of thick wire so bent as to cross the margin of the plate at a 30-degree angle. This apparently causes the leakage along the glass opposite the lead to proceed as a very long narrow salient with a smaller potential-gradient.

163. Air-cooled electromagnet for Zeeman effect. I. WALERSTEIN AND A. I. MAY (*D. E. Ross Research Fellow*), *Purdue University.* (*Introduced by K. Lark-Horowitz*).—An air-cooled electromagnet for work in Zeeman effect has been constructed due to lack of a "soft" water supply for cooling. The pattern of the instrument follows the Boas type, but includes a number of improvements. The yoke is made of a wider cross section, thus eliminating the narrowing of the pole gap upon application of the field. The current is carried by 2000 turns of flat bare copper ribbon wound in 24 pancake coils which are cooled by a forced draft of air circulated between the coils by a fan. Temperature equilibrium is reached throughout the instrument in less than an hour, and in half an hour in the pole-gap where the temperature rise is about 5°C for an inducing current of 20 amps. Using ferro-cobalt pole caps with pole face of 8 mm diameter fields of 39500 gauss and 43500 gauss were obtained respectively for gaps of 4 mm and 2.4 mm with a current of 25 amps. For a gap of 1 mm and a current of 33 amps a field of 48500 gauss was reached. Zeeman patterns were produced corresponding to nearly full strength of the magnetic field with no loss in sharpness, due to thermal fluctuations even during the first hour of application of the field.

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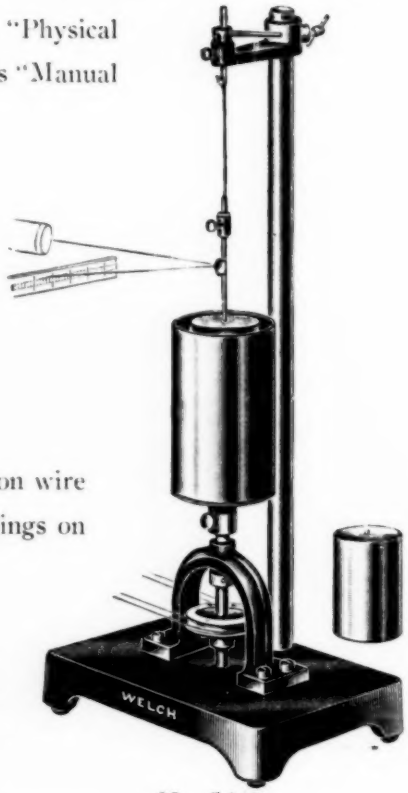

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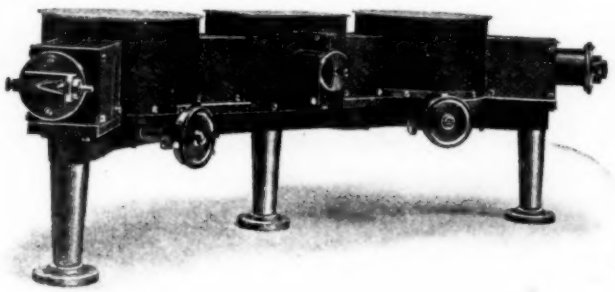

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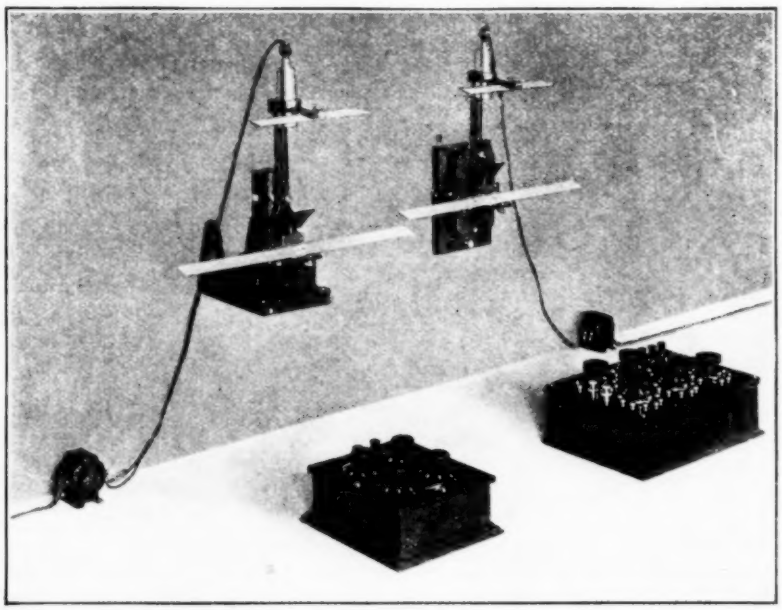

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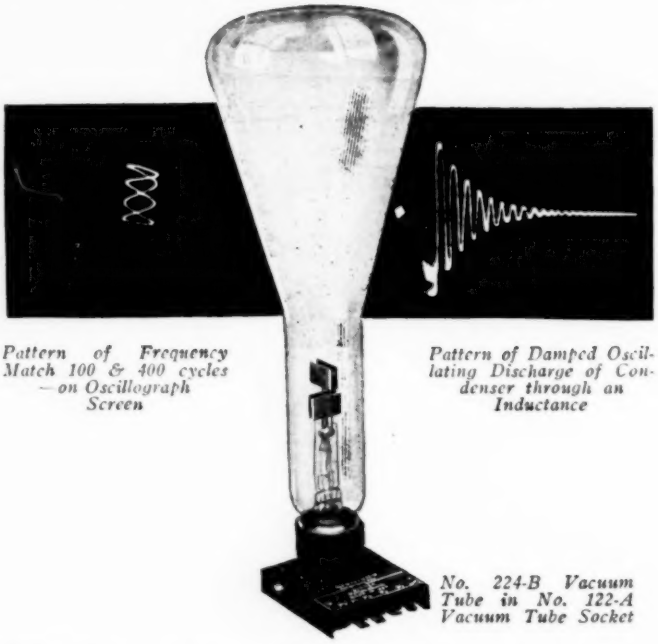

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